ECOLOGICAL INVENTORY / ASSESSMENT WORK PLAN

HI-MILL MANUFACTURING COMPANY
HIGHLAND, MICHIGAN

Revision #1 (includes modifications)

GERAGHTY & MILLER, INC.
Environmental Services

Master Copy
FINAL
(include modifications)

ECOLOGICAL INVENTORY / ASSESSMENT WORK PLAN

HI-MILL MANUFACTURING COMPANY
HIGHLAND, MICHIGAN
Revision #1 (includes modifications)

PREPARED FOR

HI-MILL MANUFACTURING COMPANY

PREPARED BY

GERAGHTY & MILLER, INC.
126 N. JEFFERSON STREET, SUITE 400
MILWAUKEE, WISCONSIN 53202
(414) 276-7742

SEPTEMBER 1991

CONTENTS

FIGURES

TABLES

APPENDIX

1.0 INTRODUCTION

This revised work plan was prepared as an addendum to conduct an ecological inventory/assessment at the Hi-Mill Manufacturing Company site and adjacent areas. Information contained in this work plan amends the October 26, 1989 Work Plan prepared by Techna Corporation (Plymouth, MI). The ecological inventory/assessment was initially presented in the draft technical memorandum submitted to the U.S. Environmental Protection Agency (USEPA) and Michigan Department of Natural Resources (MDNR) on November 15, 1990. The scope of this work plan was discussed by representatives of the USEPA and Geraghty & Miller during a pre-Quality Assurance Project Plan (QAPP) and work plan meeting on February 21, 1991. A revised sampling plan (Section 2.0) and revised QAPP (Section 8.0) were completed as addenda to the October 26, 1989 project plans. Appendix A contains the September 5, 1991 comments by the USEPA and the September 11, 1991 response by Geraghty & Miller.

An ecological inventory/assessment will be completed at the Hi-Mill Manufacturing Company site in Highland, Michigan. Results from this activity will provide decision makers with information on threats to the natural resources associated with contaminants or with actions designed to remediate the Hi-Mill Manufacturing Company site. A degree of uncertainty will be associated with these decisions. This ecological inventory/assessment is intended to reduce the inevitable uncertainty related to understanding the environmental impacts at the site and its

remediation, and to provide boundaries on the uncertainty. The ecological inventory/assessment will reduce but not eliminate uncertainty associated with the technical issues at the site.

The goal of this ecological inventory/assessment is to complete an appraisal of the actual or potential effects of the Hi-Mill Manufacturing Company site on the adjacent ecological resources. This goal is consist with the recently revised National Contingency Plan (NCP) (40 CFR 300) which calls for the identification and mitigation of environmental impacts at hazardous waste sites and the selection of remedial actions that are protective of environmental organisms and ecosystems. Several sections [e.g., 105(a)(2), 121(b)(1), 121(c), and 121(d)] of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (42 USC 9601 et seq.), as amended by the Superfund Amendments and Reauthorization Act of 1986, state that remedial actions at hazardous waste sites must be protective of human health and the environment. To achieve the goal of the ecological inventory/assessment, three principal activities will be conducted. The scope of the ecological inventory/assessment was initially presented to the USEPA and MDNR in a November 15, 1990 draft technical memorandum. The scope of the ecological inventory/assessment was later discussed with the USEPA at a pre-QAPP and work plan meeting on February 21, 1991. The ecological inventory/assessment will include an evaluation of sediment toxicity (bioassay) in Target Pond which is adjacent to the Hi-Mill Manufacturing Company site (Figure 1-1), conducting a qualitative ecological inventory of aquatic and terrestrial resources, and completing a literature survey. These activities and

associated tasks are discussed in the following sections. Prior to the discussion of the ecological inventory/assessment a brief history of recent investigative activities at the site will be provided.

1.1 History

Operations at the company began in 1946. Hi-Mill Manufacturing Company fabricates copper, aluminum, and brass (an alloy of copper and zinc) tubing parts and fittings. Production activities have included cutting, machining, forming, shaping, and soldering of the raw tubing and fabricating tubing components. Support operations have included nitric and sulfuric acid cleaning and brightening, chromic acid washing and chlorinated solvent degreasing. Prior to 1960 and continuing until 1981 process wastewater was discharged to a lagoon located immediately southeast of the Hi-Mill building. A second lagoon was constructed during 1976. In 1981 discharge to the lagoons ceased. During 1983 the sludge which had collected in the larger lagoon and surrounding soils were excavated and appropriately disposed of off-site. The MDNR provided over-sight during excavation activities.

The Hi-Mill Manufacturing Company site occupies an irregular parcel of approximately 4.5 acres. The company is bounded on the northwest by Highway M-59 (Highland Road) and on the remaining sides by the Highland State Recreation Area. Target Pond is located east of the company and is contained within the Highland State Recreation Area. Target Pond covers

approximately 8 to 10 acres. The remaining portion of the recreation area, adjacent to the company, consists of wetlands, forest, and open fields.

The Hi-Mill Manufacturing Company site was proposed for the National Priorities List (NPL) in June 1988. This action was taken by the USEPA, in part, based on available information which indicated that heavy metals from the site may have contaminated the surface water and sediment in the adjacent Target Pond.

A series of Remedial Investigation (RI) project plans were completed and approved by the USEPA and MDNR in October, 1989. During February and March 1990 surface water and sediment samples were collected from Target Pond, a drainageway from Target Pond, nearby Waterbury Lake, and a background pond located approximately 1,000 to 1,500 southeast of the company. Results from this sampling and analysis were presented in the June, 1990 RI report. The levels of three inorganic constituents in surface water samples collected from Target Pond were known to exceed the 1986 USEPA water quality criteria (USEPA Publ. No. EPA 440/5-86-001) and the MDNR Rule 57(2) guideline levels (January 30, 1990 version). The concentration of several inorganic constituents in sediment samples collected from Target Pond were higher than background levels obtained from sediment samples collected from the background pond.

In response to the November 15, 1990 draft technical memorandum and the February 21, 1991 work plan meeting, three major activities will constitute the ecological inventory/assessment. These activities will include an evaluation of sediment toxicity (bioassay) in Target Pond and Waterbury Lake, an ecological inventory, and a literature search. These activities are discussed in the following sections. Aspects of the sediment and surface sampling are discussed in the attached sampling plan (Section 2.0) and QAPP (Section 8.0). These two plans were completed as addenda to the original October 26, 1989 documents.

1.2 Bioassay

Recent analytical data collected from the sediment samples in Target Pond indicated that the levels of several inorganic constituents were higher than background levels (Appendix Y, June 21, 1990 RI report). The locations of the sediment samples collected during February 1990 are presented in Figure 1-2. The levels of aluminum, chromium, copper, and zinc in sediment samples from Target Pond were statistically above (i.e., higher than the 95% upper confidence limit for background samples) background levels. The background level was defined as the 95% upper confidence limit of the mean based on the four samples collected from the background pond. The method of establishing background concentration was calculated in accordance with MDNR guidance. Aluminum was uniformly above background in all twenty sediment samples collected from Target Pond. Levels of chromium and copper generally exceed background

concentrations in samples collected from the northeastern portion of Target Pond (Appendix Y, June 21, 1990 RI report). It should be noted that this is a general pattern because copper was detected above background in other samples (e.g., TP05 and TP09). Other sediment samples collected in Target Pond distant from the Hi-Mill Manufacturing Company (e.g., 238 mg/kg of copper at Sampling Location TP12) contained chromium and/or copper levels which exceed background levels (Figure 1-2). The concentration of zinc in the sediment sample collected from Sampling Location TP08 exceeded the background level.

During the initial RI field work samples were collected from surface sediment surface (< 1 foot deep) and from 1.5 to 2 feet below the sediment surface at five locations (Appendix X, June 21, 1990 RI report). The sediment samples containing chromium, copper, and zinc above background levels were all surficial samples. In every situation except one (208 mg/kg of zinc at Sampling Location TP08), the concentration of aluminum, chromium, copper, nickel, and zinc was higher in the surficial sediment samples (Table 1-1).

Based on this horizontal and vertical distribution of inorganic constituents in Target Pond, future investigative activities will focus on the surficial sediments in the northeastern portion of Target Pond (Figure 1-3). Three additional surficial sediment samples will be collected from the northeastern portion of Target Pond while the fourth sample will be collected from the east-central portion of the pond. The three samples from the northeastern portion of Target Pond,

near the Hi-Mill Manufacturing facility, are intended to represent potential "hot spots" where the concentration of inorganic constituents would be highest. Two background samples will be collected from the southern portion of nearby Waterbury Lake (not shown on Figure 1-3).

Additional information on the levels and actual ecological impact of inorganic constituents in the sediments of Target Pond is required for two reasons. First, just because the levels in Target Pond are statistically above background levels (i.e., higher than the 95% upper confidence limit for background samples) does not necessarily mean that an adverse ecological impact has occurred. Second, measurements of total or bulk concentrations in sediment does not provide information of the bio-availability or toxicity of the constituents. To evaluate the actual ecological impact in Target Pond a sediment toxicity evaluation (bioassay) and additional chemical characterization of the sediments will be completed. Four sediment samples will be collected from Target Pond and two sediment samples will be collected from Waterbury Lake. The bioassays will provide a direct empirical assessment of sediment quality in Target Pond. The tasks associated with the bioassay will include:

(1) A sediment toxicity evaluation of samples from Target Pond and Waterbury Lake will be conducted using a 10-day static bioassay procedure with *Hyalella azteca*

(2) Determining the concentration of inorganic constituents on the USEPA Target Analyte List (TAL) in sediment samples collected from Target Pond and Waterbury Lake.

(3) Determining the temperature, pH, moisture content (total solids), total organic carbon, and grain size distribution of the sediment samples collected from Target Pond and Waterbury Lake. These parameters can influence the mobility or bio-availability of inorganic constituents in sediment.

(4) Determine if a relationship exists between the concentration of inorganic constituents in the sediment samples and results of the bioassay.

The specific procedures to collect the sediment samples are discussed in the attached sampling plan (Section 2.0). The bioassay procedure and chemical analyses for the sediment samples are discussed in the attached QAPP (Section 8.0).

1.3 Ecological Inventory

A qualitative ecological inventory will be completed of the Hi-Mill Manufacturing Company site and adjacent areas. The ecological inventory will consist of a terrestrial survey

(Section 1.3.1) and an aquatic survey (Section 1.3.2). In addition to these surveys natural resource trustees and other technical specialists will be contacted to determine if threatened or endangered species exist at or near the site. A jurisdictional wetlands delineation will not be conducted at this time. Depending on the final remedy selected for the site, a jurisdictional wetlands delineation may be conducted before the remedial design process is completed. Areas adjacent to the site are classified as wetlands on the National Wetlands Inventory map for the area. The following two sections provide a discussion of the terrestrial and aquatic surveys.

1.3.1 Terrestrial Inventory

A qualitative terrestrial inventory will be conducted at the Hi-Mill Manufacturing Company site. The area of the terrestrial survey will be bounded on the south by Waterbury Lake and the North Arm of Waterbury Lake, on the east by Highway M-59, and on the west by Target Pond. The approximate limits of the terrestrial survey are indicated on Figure 1-3.

The presence of animals at the site will be evaluated by recording different signs. This will include but is not limited to birdnests, tracks, birdsongs, runways, and droppings. The field staff conducting the terrestrial survey will walk a number of transects to characterize the major terrestrial communities. The number and location of the transects will be determined by the field staff in cooperation with the USEPA. The field work associated with the ecological

inventory/assessment will be conducted during a few days and observation stations will not be established. The credentials of the field staff conducting the survey will include graduate training in terrestrial ecology. If appropriate university faculty members (University of Wisconsin and University of Michigan) will be consulted to make certain correct field identifications are completed. The university faculty members will have extensive experience in the identification of fauna and flora in eastern Michigan. The fauna and flora will be identified to the lowest practical taxonomic level. Woody plants will be identified to species and the forbs and grasses will be identified to genus.

In general the inventory will consist of a description of the major terrestrial biotic communities on-site and adjacent to the site. Biotic communities or habitats will be characterized by the type and relative abundance of flora and fauna they contain. In addition, a limited evaluation of potential stressed communities not related to site contaminants will be conducted. Field observations and estimates will be conducted in as consistent a manner as possible throughout the various biotic communities across the site.

The objective of the terrestrial inventory is to gather qualitative information on the ecological communities present (or expected) at the site, the potential and probable pathways by which biological receptors could be exposed to media containing site-related constituents;

identification of probable and potential biotic receptors and any readily apparent evidence of stress on biological receptors at the site.

The survey will identify which major communities exist or are expected to exist at the site. Habitat models will not be used. Also a detailed inventory of pre-settlement communities or surveyor notes will not be consulted. The U.S. Soil Conservation Service County Soil map will be reviewed and incorporated into the survey. A general list of plants and animals expected to occur at the site will be developed from a review of readily available literature on the terrestrial communities of eastern Michigan. Based on this review of previously published information, no effort will be made to abbreviate the lists of species.

The information gathered during the ecological inventory will be used to provide site-specific information on:

(1) the general occurrence and distribution of flora and fauna observed at the site (and expected to occur at the site) and characterize terrestrial receptors

(2) the general diversity of major terrestrial communities at the site

(3) occurrence of potentially sensitive and important ecological resources at the site.

The data (i.e., location of habitats, observations and estimates of flora and fauna diversity of major terrestrial communities) obtained from the ecological inventory will provided important information that will be used to prepare the baseline risk assessment, and establishing site food chains and receptors.

A qualitative terrestrial assessment will be completed and the results presented in a narrative form. A quantitative survey (e.g., hard data) will not be completed during this phase of the assessment. A descriptive assessment of floral diversity will be provided. Major terrestrial communities will consist of areas containing relatively homogenous flora and associated fauna. A specific criteria for the definition of major terrestrial communities is not provided, however, we anticipate that fewer than ten major communities will be encountered at the site. During the site visit the presence of minor terrestrial communities, some of which might be rare, will be described if they are present.

The investigative approach for the terrestrial inventory will include a number of procedures. The identification of major floral communities and characterization of vegetative species within each community will be completed. A literature review will be conducted to determine flora and fauna communities expected to be present on-site and immediately surrounding the site. A preliminary review of existing maps, soil reports, etc. to identify drainage patterns, soil types, mapped wetlands topographic features, etc. will be conducted prior

to initiating field work. Major upland and potential wetland communities will be identified on the most currently available aerial photograph. The upland communities will be categorized as being either forested, shrub, or open field. The extent of coverage in acres and location of each of these community types will be estimated from the aerial photograph. The field evaluation will consist of verifying the coverage estimates and vegetative community locations. Observations and identification of vegetative species within each defined communities and an estimate of general abundance of plant species within each strata (herb, shrub, and trees) will be recorded. An estimate of the relative age and size distribution of trees will be recorded. The relative age of the trees can be estimated by measuring their diameter at breast height (DBH). The growth of trees near the site may have been attenuated resulting in an underestimation of relative age based on DBH. The age of six trees at the site will also be estimated by taking small-diameter cores from their trunks and counting the number of growth rings. The age of the trees, based on the growth rings, will be related to the DBH. To establish this relationship cores will be collected from three impacted trees near the site and taking cores from three trees in an unimpacted area. The holes in the trunks will be filled with sealant. The trees selected for this work will be of the same species and growing in similar environments. Qualitative observations of soil flora and fauna (including the litter layer depth, if present) will be recorded. Field identification of environmental processes that affect the fate and transport of site-specific constituents along with an identification of potential media of transport will be performed. This

field identification will be focused but not limited to those areas of the site with known site-specific constituents.

1.3.2 Aquatic Inventory

Recent analytical data collected from the surface water samples in Target Pond indicated that the levels of three inorganic constituents exceeded the USEPA water quality criteria and the MDNR Rule 57(2) guideline levels (Appendix W, June 21, 1990 RI report). Specifically, the concentrations of copper, nickel, and silver in surface water samples from Target Pond exceeded the regulatory criteria (Table 1-2). Inspection of the analytical results revealed that the maximum concentration of copper in the background pond also exceeded the regulatory criteria. The maximum concentration in the surface water sample from Target Pond was 9% higher than the maximum concentration of copper observed in the background pond. The maximum concentration of silver in the background pond was greater than the maximum concentration observed in Target Pond. Fifteen surface water samples were analyzed for levels of nickel. Of the fifteen samples, ten were qualified as estimated concentrations because the duplicate sample results were not within control limits. An obvious spatial pattern in the nickel concentrations from surface water samples in Target Pond was not apparent. For example, nickel was not detected in two surface water samples (Sampling Locations TP07 and TP11, Figure 1-2) collected adjacent to the Hi-Mill Manufacturing Company site. The highest observed nickel

concentration in Target Pond was from a sample (TP09, Figure 1-2) collected approximately 400 feet from the Hi-Mill Manufacturing Company site in the southern portion of Target Pond.

Previously, surveys of Target Pond were conducted by the MDNR. These results indicated that selected inorganic constituents were elevated in surface water samples collected from Target Pond. This chemical information is considered qualitative and does not necessarily support changes in concentrations over time. In the absence of cross calibration, of appropriate standards, and of inter-laboratory comparison such long-term data should be viewed cautiously. For example, Shapiro and Swain (Science, 221: 457-9) provide a critical review of the apparent long-term silica decline in Lake Michigan. The authors concluded that the apparent decline was actually the result of changes in sampling and analytical methods used over a period of years.

One interesting aspect of the 1984 MDNR survey was the apparent absence of adverse impact to the phytoplankton, zooplankton, and macrophytes in Target Pond. Mr. David Kenaga, the author of the 1984 survey, reported that *Daphnia* were very abundant at the sampling site nearest the Hi-Mill Manufacturing Company. The copper concentration in the surface water sample from that location exceeded criteria for aquatic life. Mr. Kenaga went on to state that *Daphnia* is generally considered sensitive to relatively low copper concentrations. The copper in Target Pond could be sequestered in a form that is not toxic to *Daphnia*. *Daphnia* could become concentrated along the margin of Target Pond. Zooplankton tend to accumulate on the

leeward side of lakes whenever a fairly strong wind persists for an appreciable period of time. Wind direction, velocity, and duration immediately before the MDNR sampling were not reported. Also, it is not known if the fetch and orientation of Target Pond is sufficient to allow significant hydrographic water movements. The wind-induced movement of zooplankton, if it occurs in Target Pond, is a relatively slow process. It is not likely that zooplankton could be slowly transported to an area of Target Pond containing toxic levels of a constituent and remain viable. The proposed ecological inventory/assessment will provide information on the occurrence, composition and relative health of the zooplankton community at several locations in Target Pond. Once this information is available, an assessment of aquatic impacts will be completed. The 1984 MDNR survey also reported that chironomid midges were present in the sediments of Target Pond. A detailed investigation of the benthic macroinvertebrates inhabiting the sediments was not completed, however, midges are generally considered to be relatively tolerant of metal-contaminated sediments. In conclusion Mr. Kenaga stated that the presence of variety of filamentous green algae (*Spirogyra*), flagellates (*Euglena*) and other algae (*Scenedesmus, Oocystis, Synedra, Oscillatoria*, and *Mougeotia*) and macrophytes (*Typha, Scripus, Lemna minor, Elodea*, and *Potomageton*) indicated that the discharge (from the former lagoon) did not have much impact on these aquatic plants.

Additional information on the aquatic communities of Target Pond is required. This will consist of assessing the relationship between the previously described water quality of Target

Pond (presented in the June 21, 1990 RI Report and MDNR data) and any qualitative changes in the aquatic community between Target Pond and Waterbury Lake, a control site. Samples will be collected during a single sampling event from the same four sites in Target Pond and two locations in Waterbury Lake where the sediment sampling will be conducted (Figure 1-3). The tasks associated with the aquatic inventory will included:

(1) Completing a qualitative survey of the phytoplankton, zooplankton, and benthic macroinvertebrates in Target Pond and Waterbury lake.

(2) Determining if qualitative changes in the phytoplankton, zooplankton, and benthic macroinvertebrate community exist between Target Pond and Waterbury Lake. Specific comparisons within Target Pond and between Target Pond and Waterbury Lake for the phytoplankton, zooplankton, and benthic macroinvertebrate assessments will include a tabular and graphic presentation of the results. These presentations will include information such as a list of taxa, number of individuals, relative abundance, and tolerance to contamination. A narrative description of the results will be provided in which qualitative changes (if present) will be discussed. Dr. Meier (University of Michigan, Ann Arbor, MI) will provide an assessment of the relative tolerance of specific aquatic organisms to contaminants.

The specific procedures to collect the surface water samples are discussed in the attached sampling plan (Section 2.0)

1.4 Literature Search

A number of trees near Sampling Locations TP08 and 11 (Figure 1-2) have died. The reason for these trees dying is not known. To evaluate whether the observed concentrations of inorganic constituents in the soil and sediment samples could have killed the trees a literature search will be conducted. A number of databases will be searched for toxic impacts to trees caused by reported concentrations of inorganic constituents in the adjacent soil and sediment. This information will include (if available) bioaccumulation potential, uptake rates, bioconcentration factors for flora and fauna.

The Aquatic Toxicity Information Retrieval System (AQUIRE) is maintained by the USEPA Environmental Research Laboratory in Duluth, Minnesota. A search of this data base will be completed using one of two commercial services. The actual search will be conducted by Chemical Information Systems (CIS) or Technical Database Services.

Personnel at the Duluth laboratory stated that AQUIRE might not contain the most recently available literature. Depending on the search results using AQUIRE additional

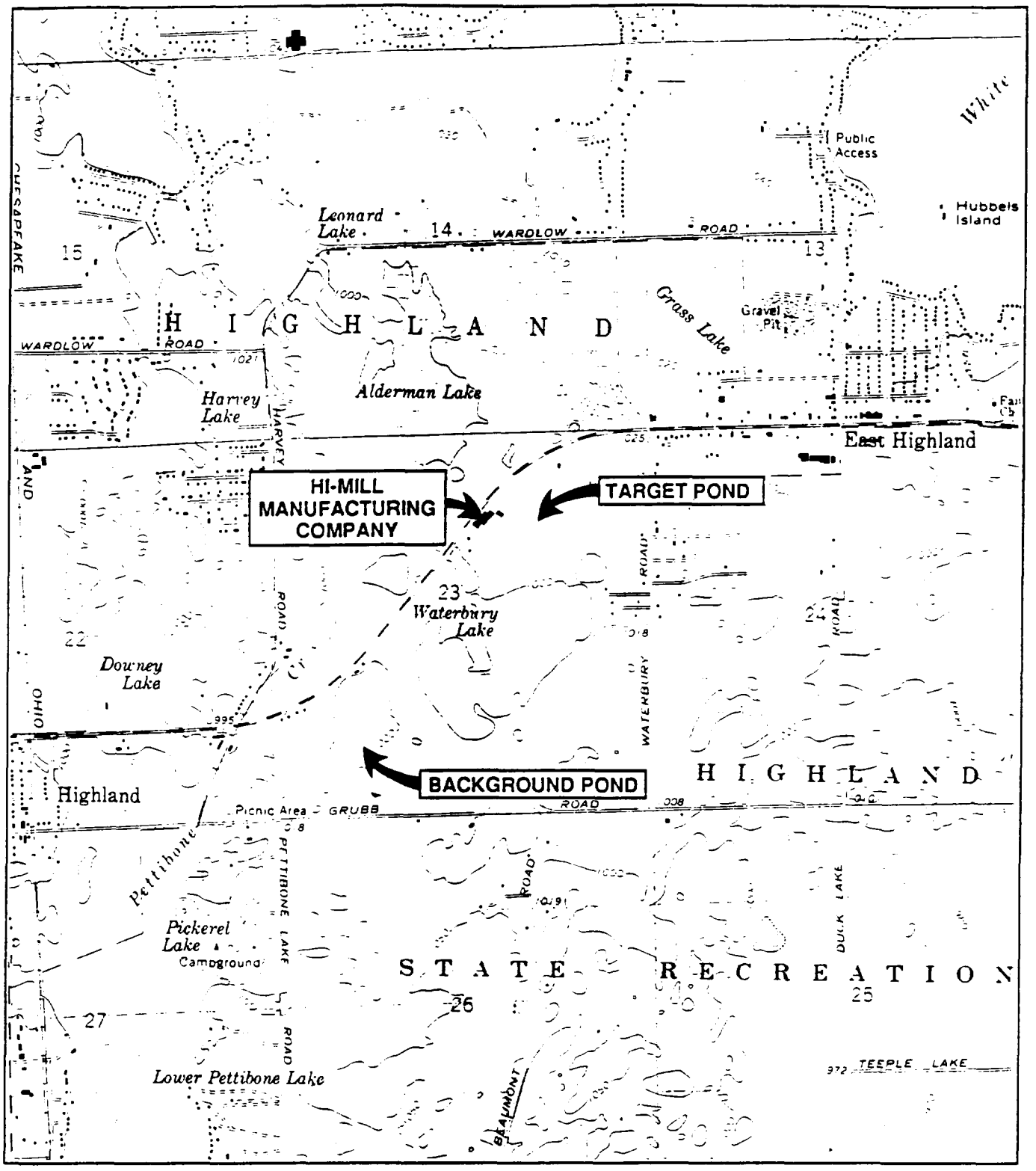
databases may be searched. These databases may include Biological Abstracts, Bios, Chemical Abstracts, Pollution Abstracts, Aquatic Sciences and Fisheries Abstracts, and the National Technical Information Service (NTIS). These databases will be accessed through the University of Wisconsin.

1.5 Summary

Information generated during the ecological inventory/assessment will be included in the RI report which is scheduled to be completed in July 1991. This information will help to define the nature and extent of contamination at the site. Actual and potential adverse ecological impacts associated with contaminants at the site will also be included in the RI report. Components of the ecological inventory/assessment will be used to address important exposure pathways and environmental receptors at the site. This material will be incorporated in the baseline risk assessment. Aspects of the ecological inventory/assessment will be included during the screening of potential remedies for the site.

832HIMILL/workplan.

FIGURES

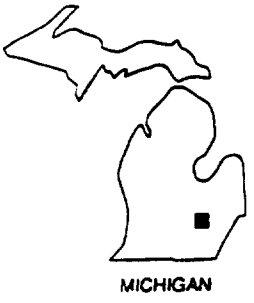


SOURCE: USGS 7.5 Minute Topographic Map, HIGHLAND, MICHIGAN Quadrangle 1983

N

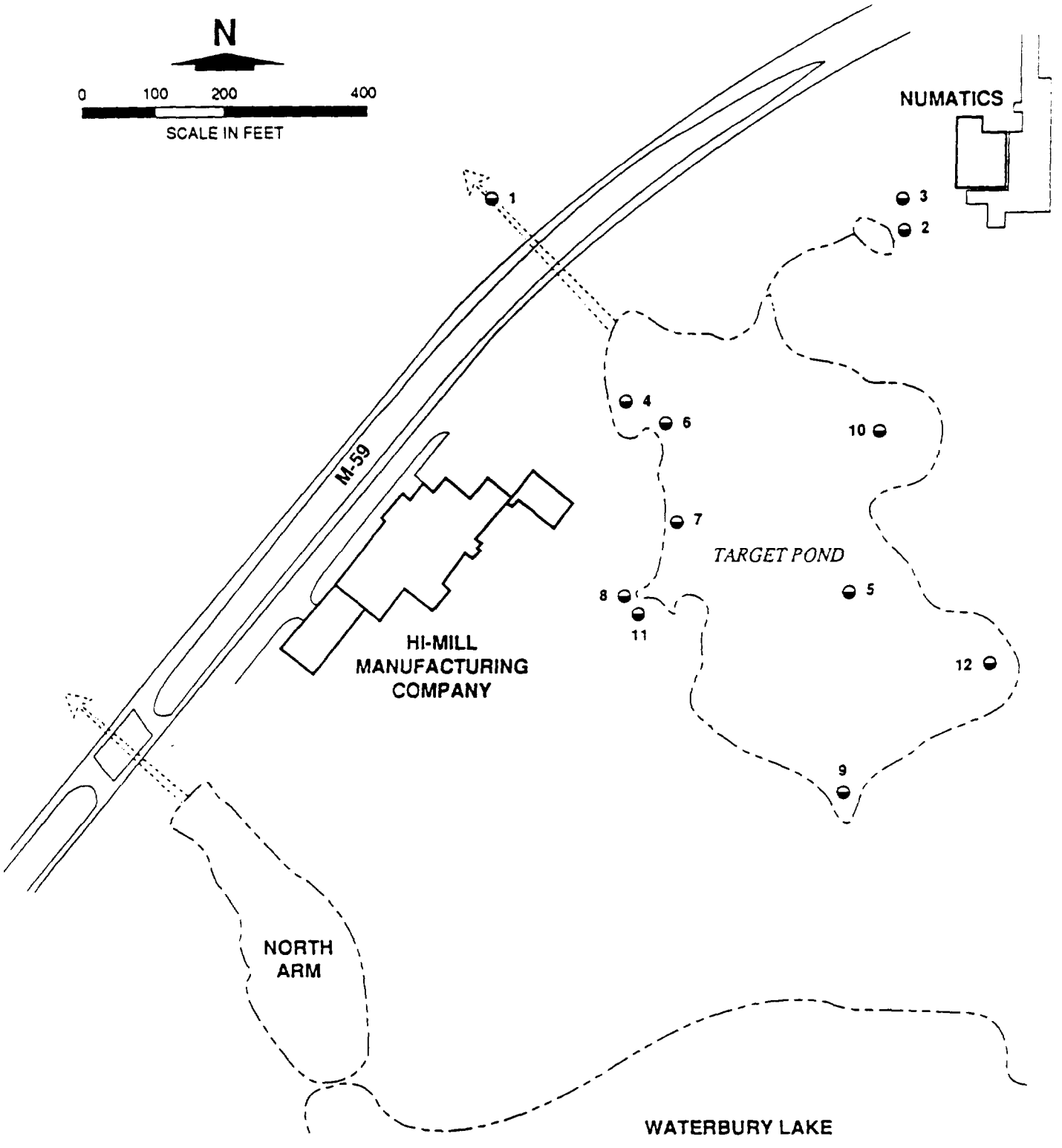
0 1000 2000 4000

SCALE IN FEET



GERAGHTY & MILLER, INC.
Environmental Services

FIGURE 1-1
SITE LOCATION MAP
HI-MILL MANUFACTURING COMPANY
HIGHLAND, MICHIGAN
MI135.04 - 0144 04

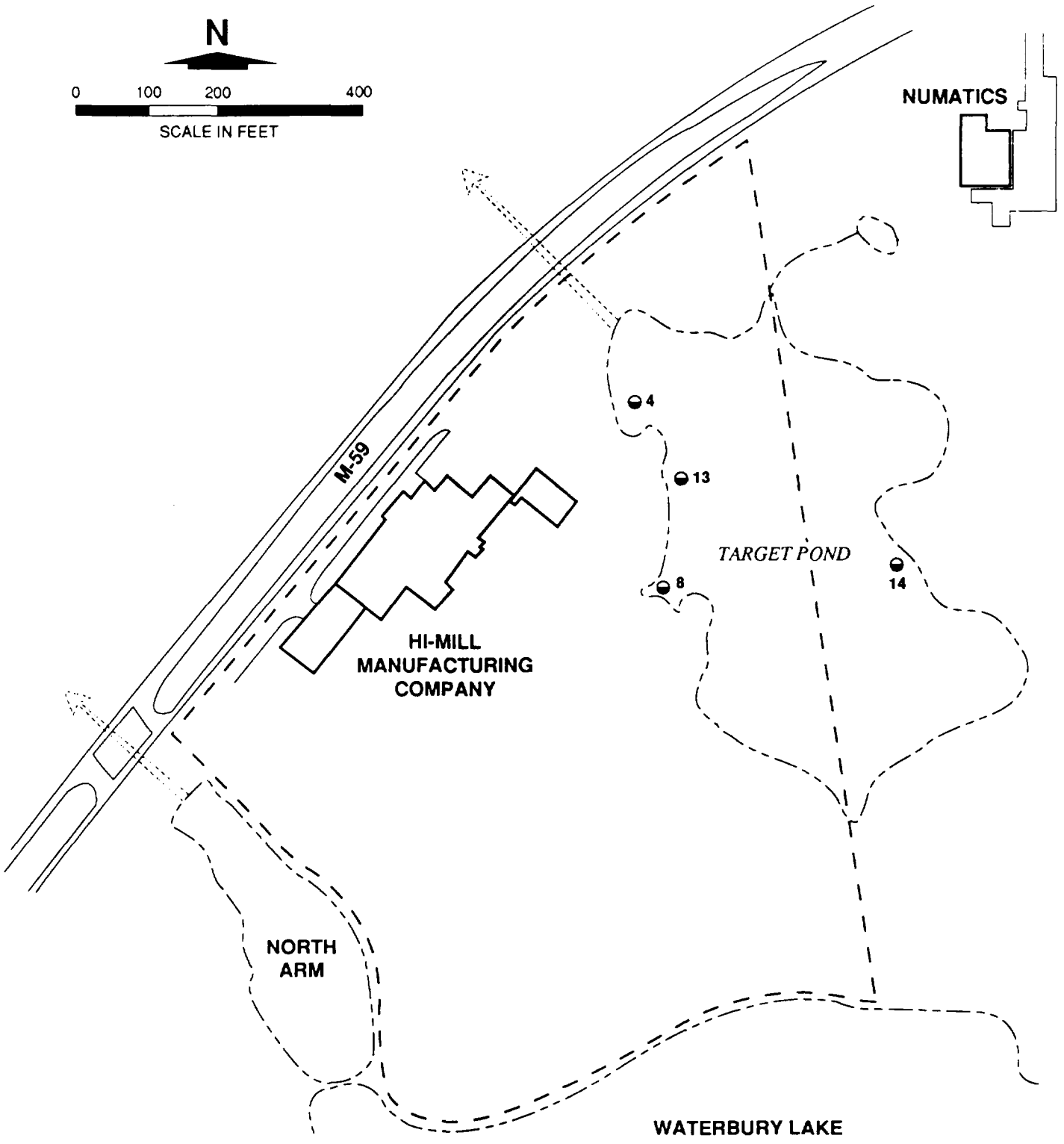


LEGEND

● 1 SEDIMENT AND SURFACE WATER SAMPLING LOCATION

GERAGHTY & MILLER, INC.
Environmental Services

FIGURE 1-2
SEDIMENT AND SURFACE WATER SAMPLING LOCATIONS
(FEBRUARY - MARCH 1990)
HI-MILL MANUFACTURING COMPANY
HIGHLAND MICHIGAN
MI135.04 - 0144.03



LEGEND

- ◒ 8 — **SEDIMENT AND SURFACE WATER SAMPLING LOCATION**
- — — — **LIMITS OF TERRESTRIAL SURVEY**

NOTE : SAMPLE 15 AND 16 WILL BE COLLECTED FROM SOUTHERN PORTION OF WATERBURY LAKE

FIGURE 1-3
PROPOSED SEDIMENT AND SURFACE WATER SAMPLING LOCATIONS
HI-MILL MANUFACTURING COMPANY
HIGHLAND MICHIGAN
MI135.04 - 0144.05

GERAGHTY & MILLER, INC.
Environmental Services

Table 1-1 Comparison Between Inorganic Concentrations in Surficial Sediment Samples and Sediment Samples Collected at Depth.

Sampling Locations[a]	Inorganics (mg/kg)							
	Al	Cr	Cu	Ni	Ag	Zn	Cr(+6)	% Solids
TP04	28,400	145	429	41.9	<4.1	10.4	<0.22	45.4
TP04-1	11,800	24.9	18.4	28.2	<2.2	5.4	<0.12	82.3
TP06	21,500	36.2	64.8	20.1	<3	51.5	<0.17	58.2
TP06-1	15,300	25.4	7	27.8	<2.2	52.5	<0.12	83.1
TP07	27,800	50.9	105	27	<3.2	82	<0.19	53.4
TP07-1 (Avg.)	14,950	26.7	13.1	26.3	<2.3	54	<0.13	79.1
TP08	28,600	256	982	33.1	<3.1	208	<0.18	55.7
TP08-1	15,500	30.5	6.6	30.6	<2.2	53.1	<0.12	8.2
TP11	21,500	974	1860	22.8	<2.6	65.3	<0.15	67.2
TP11-1	13,800	32	15.1	22.7	<2.3	41.1	<0.12	79.6

a = Sampling locations from Target Pond; surficial sediment (e.g., TP04) and sediment collected from 1.5 to 2 feet below the sediment surface (e.g., TP04-1). See Figure 2-1 of the June 21, 1990 draft Remedial Investigation report for specific sampling locations.

= The concentration in the sediment sample (TP06-1) collected at depth exceeded the concentration in the surficial sediment sample.

Notes:

(1) Sample results taken from the June 21, 1990 draft Remedial Investigation report.

(2) A duplicate sample was collected from TP07-1 and the average concentrations are presented.

(3) The concentration of zinc in TP06-1 did not exceed the background level. The only sample to exceed background levels for Zinc was TP08.

832hi-mill/compar.wk1

Table 1-2. Comparison Between Regulatory Criteria and Maximum Work Plan Concentrations of Inorganic Constituents in Surface Water Samples.

Inorganics	Reporting Limits	USEPA Criteria	MDNR Rule 57(2)	Maximum Concentrations Background Pond	Maximum Concentrations Target Pond
Aluminum	200	NS	NS	<85	5,360
Antimony	60	610	NS	65.4	<61
Arsenic	10	190	184	<3	<3
Barium	200	NS	NS	<42	<42
Beryllium	5	5.3	NS	<1	<1
Cadmium	5	1.36	0.5	<2	<2
Calcium	5,000	NS	NS	26,500	44,500
Chromium (+3)	10	250	58	9.3*	28.5*
Cobalt	50	NS	NS	<14	<14
Copper	25	14	13	19.5	21.4
Iron	100	1,000	NS	<39	402
Lead	3	4	4	3.3	3.5
Magnesium	5,000	NS	NS	5,050	11,500
Manganese	15	NS	NS	7.3	625
Mercury	0.2	0.012	NS	<0.2	<0.2
Nickel	40	114	41	17.8*	302*
Potassium	5,000	NS	NS	817	3,880
Selenium	5	35	20	<1	<1
Silver	10	6	0.1	12.5	11.4
Sodium	5,000	NS	NS	2,620	26,000
Thallium	10	NS	NS	<4	<4
Vanadium	50	NS	NS	<8	<8
Zinc	20	389	60	12.4	16.2
Cyanide	10	5.2	4	<10	<10
Chromium (+6)	10	11	3	<10	<10
Ammonia	50	NS	NS	160	--
Nitrate/Nitrite	50	NS	NS	180	<50

[ ] = Reporting limit greater than USEPA Criteria and MDNR Rule 57(2).

[ ] = Concentration exceeds USEPA Criteria and MDNR Rule 57(2).

Reporting Limits - approved October 26, 1989 QAPP (Table 8-2).

USEPA Criteria - Water Quality Criteria for Water (EPA 440/5-86-001).

MDNR Rule 57(2) - Guideline levels, January 30, 1990.

Maximum concentrations - June 21, 1990 RI report.

Hardness-dependent values based on average hardness of 126 mg/L for Target Pond.

NS = No standard.

* = Duplicate values not within quality control limits, values are estimated.

832HIMILL/unname.wk1

APPENDIX A

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
230 SOUTH DEARBORN STREET
CHICAGO, IL 60604

REPLY TO THE ATTENTION OF:

5HS-11

September 5, 1991

Mr. Kevin K. Wolka, P.E., Ph.D.
Geraghty & Miller, Inc.
50 W. Big Beaver Road
Troy, Michigan 48084

Dear Mr. Wolka:

The following are comments on the Ecological Inventory/Assessment Workplan. They are issues that need to be clarified before field work is begun. In an effort to avoid delay and make addressing these issues as brief and quick as possible, the U.S. EPA is only requesting that the comments be addressed in a letter. The letter will then be included as an addendum to the workplan before it is approved.

Section 1.0

Page 9, Paragraph 2:

The workplan states that the terrestrial survey will include areas adjacent to the site. What exactly are the boundaries of the terrestrial survey?

It is stated that "Field observations and estimates will be conducted in as consistent a manner as possible throughout the various biotic communities across the site". With the exception of stating that size and frequency of trees will be recorded, little information on what observations will be made in the field with respect to the fauna present is provided. What type of animal sign will be recorded? Will the walkover be conducted in a systematic way, i.e. will transects be walked? Observation stations established? What will be the credentials of the personnel performing the walkover? There are not many individuals with the ability to do adequate field identifications of diverse biotic groups. That is, not many individual botanists or zoologists are capable of doing field identifications of plants, terrestrial macroinvertebrates (to the family or genus level), vertebrates and vertebrate sign. There is also a lack of clarity as to what level organisms will be identified. You discuss that plant communities will be classified as trees, shrubs, and herbs, yet the species

composition of the communities could be important. Woody plants should be identified to species, while forbs and grasses should be identified to genus. In general, the terrestrial survey procedures and specific endpoints should be outlined in more detail.

Page 9, Paragraph 3:

The terrestrial survey is intended to identify what communities exist at the site, or are expected to exist. How will you determine what communities are "expected"? Will habitat models be used? If so, which ones? The statement on page 11 of Section 1.0, that this determination will be made based on a literature review does little to answer this question. For example, will the literature review be an attempt to survey historical records and publications to see what communities were actually present in pre-settlement times? Will it be a review of surveyor notes to determine surveyor descriptions and relative frequency and type of witness trees (if trees were present)? Will it be a survey of soil types to determine what flora may grow, or may have grown, in these types? Will it be a survey of plant communities with respect to the fauna associated with them? Will it be the frequently employed technique of reviewing state faunal lists and field guides to identify every animal species whose range includes the site? If the method employed is the latter one, what criteria will be used to cull species from the lists that are not likely to be present?

Page 10, Paragraph 3:

The paragraph results in three questions: 1)What data? Little hard data are proposed for collection with respect to the terrestrial inventory; 2) What kind of estimate of diversity is going to be made? and 3) What criteria defines a "major terrestrial community"? Does question (3) imply that "minor terrestrial communities" will not be defined? Might not some of these be locally rare?

Page 11, Paragraph 1:

How will the relative age of the trees be estimated, by their diameter at breast height (DBH)? The Hi-Mill facility began operating in 1946, almost 50 years ago. If the facility had a negative impact on the growth rates of the trees of the surrounding area, the DBH could be a poor indicator of tree age, giving the impression of a much younger population of trees. Such a finding could lead to the misleading conclusion that tree population recruitment is good. The possibility that tree growth could be affected is underscored by the acknowledgement on Page 15 of Section 1.0, that a number of trees at the site have died of unknown causes.

Page 13, Paragraph 2:

The explanation that the Daphnia population found be the MDNR was blown in from a different part of Target Pond is a plausible one. You should state why they think it is unlikely.

If you have any questions, please feel free to contact me at (312) 886-5993.

Sincerely,

Karla L. Johnson
Remedial Project Manager

cc: Steve Ellingson, Geraghty & Miller

GERAGHTY & MILLER, INC.
Environmental Services

Ground Water *Engineering* *Hydrocarbon* *Remediation* *Education*

September 11, 1991

Karla L. Johnson
U.S. Environmental Protection Agency
230 Dearborn Street
Chicago, Illinois 60604

RE: Response to comments on the Revised Hi-Mill Ecological Inventory/Assessment Work Plan, Highland, Michigan

Dear Ms. Johnson:

We have prepared a series of responses to your September 5, 1991 comments on the June 7, 1991 revised workplan. Most of the comments by the U.S. Environmental Protection Agency (USEPA) were related to the proposed terrestrial survey. The survey is intended to provide a general characterization of the predominate terrestrial communities at the site. A detailed inventory of the flora and fauna will not be completed. The purpose of the survey is to determine if constituents from the Hi-Mill Manufacturing Site have adversely impacted or pose a risk to the environment. An assessment of sufficient complexity will be completed to address the issues of environmental impacts or risks. If the initial results of the survey indicate that environmental impacts or risks are significant a more focused terrestrial survey will be completed.

The following paragraphs contain our responses to your comments. It is our understanding these responses will constitute an addendum to the June 7, 1991 work plan. The USEPA has not requested that another revision to the work plan be submitted.

Section 1.0
Page 9, Paragraph 2:

The area of the terrestrial survey will be bounded on the south by Waterbury Lake and the North Arm of Waterbury Lake, on the east by Highway M-59, and on the west by Target Pond. The approximate limits of the terrestrial survey are indicated on Figure 1.

The presence of animals at the site will be evaluated by recording different signs. This will include but is not limited to birdnests, tracks, birdsongs, runways, and droppings. The field staff conducting the terrestrial survey will walk a number of transects to characterize the major terrestrial communities. The number and location of the transects will be determined by the field staff in cooperation with the USEPA. The field work associated with the ecological inventory/assessment will be conducted during a few days and observation stations will not be established. The credentials of the field staff conducting the survey will include graduate training

in terrestrial ecology. If appropriate university faculty members (University of Wisconsin and University of Michigan) will be consulted to make certain correct field identifications are completed. The university faculty members will have extensive experience in the identification of fauna and flora in eastern Michigan. The fauna and flora will be identified to the lowest practical taxonomic level. Woody plants will be identified to species and the forbs and grasses will be identified to genus.

Page 9, Paragraph 3:

The survey will identify which major communities exist or are expected to exist at the site. Habitat models will not be used. Also a detailed inventory of pre-settlement communities or surveyor notes will not be consulted. The U.S. Soil Conservation Service County Soil map will be reviewed and incorporated into the survey. A general list of plants and animals expected to occur at the site will be developed from a review of readily available literature on the terrestrial communities of eastern Michigan. Based on this review of previously published information, no effort will be made to abbreviate the lists of species.

Page 10, Paragraph 3:

A qualitative terrestrial assessment will be completed and the results presented in a narrative form. A quantitative survey (e.g., hard data) will not be completed during this phase of the assessment. A descriptive assessment of floral diversity will be provided. Major terrestrial communities will consist of areas containing relatively homogenous flora and associated fauna. A specific criteria for the definition of major terrestrial communities is not provided, however, we anticipate that fewer than ten major communities will be encountered at the site. During the site visit the presence of minor terrestrial communities, some of which might be rare, will be described if they are present.

Page 11, Paragraph 1:

The relative age of the trees can be estimated by measuring their diameter at breast height (DBH). The growth of tress near the site may have been attenuated resulting in an underestimation of relative age based on DBH. The age of six tress at the site will also be estimated by taking small-diameter cores from their trunks and counting the number of growth rings. The age of the trees, based on the number of growth rings, will be related to the DBH. To establish this relationship cores will be collected from three impacted trees near the site and taking cores from three trees in an unimpacted area. The holes in the trunks will be filled with sealant. The trees selected for this work will be of the sample species and growing in similar environments.

Page 13, Paragraph 2:

Daphnia could become concentrated along the margin of Target Pond. Zooplankton tend to accumulate on the leeward side of lakes whenever a fairly strong wind persists for an appreciable period of time. Wind direction, velocity, and duration immediately before the MDNR sampling were not reported. Also, it is not known if the fetch and orientation of Target Pond is sufficient to allow significant hydrographic water movements. The wind-induced movement of zooplankton, if it occurs in Target Pond, is a relatively slow process. It is not likely that zooplankton could be slowly transported to an area of Target Pond containing toxic levels of a constituent and remain viable. The proposed ecological inventory/assessment will provide information on the occurrence, composition and relative health of the zooplankton community at several locations in Target Pond. Once this information is available an assessment of aquatic impacts will be completed.

We believe that our responses to your comments are complete, and will clarify our proposed inventory/assessment. We would appreciate a timely review and approval of the work plan. As discussed, field work to complete this portion of the project is scheduled to begin during the week of September 16. If you have any questions, regarding the responses, please do not hesitate to contact us.

Respectfully Submitted
Geraghty & Miller, Inc.

Stephen B. Ellingson
Principal Scientist/Office Manager

Kevin K. Wolka, P.E., Ph.D.
Principal Scientist/Project Coordinator

xc: Deborah D. Larson, MDNR
Robert F. Beard, Hi-Mill
Richard W. Beard, Hi-Mill
Robert C. Davis, Butzel Long et al.
Laurie Hellmer, Geraghty & Miller, Chicago
Todd Udvig, Geraghty & Miller, Madison
Frank Jones, Geraghty & Miller, Raleigh
Murat Akyurek, Donohue & Associates
Hi-Mill Subcontractors

SECTION 2.0
REMEDIAL INVESTIGATION SAMPLING PLAN ADDENDUM
REMEDIAL INVESTIGATION/FEASIBILITY STUDY
HI-MILL MANUFACTURING COMPANY
Highland, Michigan

Prepared by:

GERAGHTY & MILLER, INC.
126 N. Jefferson St.
Suite 400
Milwaukee, WI 53202

September, 1991

CONTENTS

Page

FIGURES

2.0 REMEDIAL INVESTIGATION SAMPLING PLAN

This revised sampling plan was prepared as an addendum to collect sediment and surface water samples for subsequent laboratory analysis as part of the ecological inventory/assessment of Target Pond and Waterbury Lake. Information contained in this sampling plan addendum amends the October 26, 1989 sampling sample prepared by Techna Corporation (Plymouth, MI). The scope of this sampling was discussed by representatives of the U.S. Environmental Protection Agency (USEPA) and Geraghty & Miller during a work plan meeting on February 21, 1991.

2.1 Introduction

This revised sampling plan was prepared to provided a detailed description of field activities proposed for the Hi-Mill Manufacturing Company site. The purpose and methodology of the surface water and sediment sampling is outlined.

During February and March 1990 a series of surface water and sediment samples were collected from Target Pond, Waterbury Lake, and a background pond. The location of these previous sampling sites in Target Pond is depicted in Figure 2-7. Background surface water and sediment samples were collected from a wetland with the same National Wetlands Inventory classification as Target Pond. This background pond is located approximately 1,000 to 1,500 feet southwest of the Hi-Mill Manufacturing Company site as shown in revised Figure 2-1. This sampling will focus on the area of Target Pond adjacent to the Hi-Mill Manufacturing Company site. Sediment and surface water samples will be collected from four locations in Target Pond and two locations in Waterbury Lake (revised Figure 2-5). Three of the four sediment and surface water samples will be collected from the northwestern portion of Target Pond. Two of these locations were also sampled during February and March 1990. The third sampling

location in the northwestern portion of Target Pond will be situated approximately midway between February and March 1990 Sampling Locations 6 and 7. The final surface water and sediment sampling location in Target Pond will be situated in the east-central portion of the pond.

Two surface and sediment sampling locations will be collected from the southern portion of Waterbury Lake. The samples will serve as background samples.

Specific sampling locations will be selected where the water depth, adjacent vegetation, surface water runoff areas, sediment depositional patterns, sediment texture, and sediment color are similar. The initial samples will be collected in the northwestern portion of Target Pond. The subsequent sampling locations will be as similar as practical to these initial samples. The selection process may necessitate moving the sampling sites to slightly different locations than those proposed in revised Figure 2-5. The specific sampling locations will be approved by the USEPA or their field representative prior to initiating sampling collection activities.

To minimize the disturbance of the sediment and surface water the samples will be collected from a small, shallow draft boat. The location of the specific sampling sites will be described in the field notebook and photographically documented. The water depth will be recorded and the adjacent vegetation will be described.

Direct visual bearings to prominent landmarks near the site will be recorded with a hand-held compass (or equivalent). The estimated position of the sampling sites will be where at least two lines of position intersect. A small float attached to an anchor will be left at each sampling location.

2.8 Surface Water and Sediment Sampling

A discussion of the purpose of sample collection activities and methodologies is presented in the following sections.

2.8.1 Purpose

The purpose of collecting the sediment and surface water samples is described in the following two sections.

2.8.1.1 Sediment Samples

Previous investigations conducted by the Michigan Department of Natural Resources (MDNR) and the June 21, 1990 Remedial Investigation (RI) report indicated that the concentration of selected metals in sediment samples collected from Target Pond exceeded background levels. The sediment samples from Target Pond were compared to four samples collected from a background pond located approximately 1,000 to 1,500 feet southwest of Target Pond. A series of sediment samples will be collected from Target Pond and Waterbury Lake. The purpose of this task will be to:

- confirm whether the concentrations of selected metals in sediment samples from Target Pond exceed background levels represented by samples collected from Waterbury Lake. The parametric coverage for all of the samples will be expanded over that employed during the February 1990 sediment sampling.

- determine the temperature, pH, moisture content (total solids), total organic carbon concentration, and grain size distribution of the sediment samples collected

from Target Pond and Waterbury Lake. These parameters can influence the mobility or bio-availability of metals in sediment.

- qualitatively describe the benthic macroinvertebrate communities in Target Pond and Waterbury Lake. An evaluation will be completed to determine if differences in the benthic macroinvertebrate communities exists between samples collected from Target Pond and Waterbury Lake.

- conduct a sediment toxicity evaluation (bioassay) of the samples collected from Target Pond and Waterbury Lake using *Hyalella azteca*.

- determine if a relationship exists between the concentration of metals in the sediment samples and results of the bioassays.

The methodology associated with collecting these samples is presented in revised Section 2.8.2 (Methodology). Additional information on laboratory standard operating procedures (SOPs) and quality assurance procedures is provided in the addendum to the Quality Assurance Project Plan (QAPP) (revised Section 8.0).

2.8.1.2 Surface Water Samples

Previous investigations by the MDNR and the June 21, 1990 RI report indicated that concentration of selected metals in surface water samples collected from Target Pond exceeded USEPA criteria and MDNR Rule 57(2) guideline levels (see Table 1-2 of the attached Work Plan). A series of surface water samples will be collected from Target Pond and Waterbury Lake The purpose of this task will be to:

- qualitatively describe the phytoplankton and zooplankton communities in Target Pond and Waterbury Lake. A evaluation will be completed to determine if differences in the phytoplankton or zooplankton communities exist between samples collected from Target Pond and Waterbury Lake.

The methodology associated with collecting these samples is presented in revised Section 2.8.2 (Methodology). Additional information on laboratory standard operating procedures (SOPs) and quality assurance procedures is provided in the addendum to the Quality Assurance Project Plan (QAPP) (revised Section 8.0).

2.8.2 Methodology

The field methods used to collect the sediment and surface water samples is described in the following sections. Surficial sediment samples will be collected using a grab sampler and submitted to different laboratories for chemical analysis, sediment toxicity evaluations, characterization of grain size distributions, and a qualitative assessment of the benthic macroinvertebrate community. Surface water samples will be submitted to the University of Michigan for a qualitative evaluation of the phytoplankton and zooplankton communities.

2.8.2.1 Sediment Sampling

A brief reconnaissance of the area conducted in October 1990 indicated that the littoral zone of Target Pond and Waterbury Lake consist of emergent macrophytes (e.g., *Typha*). At several locations floating-leaved macrophytes (e.g., *Nuphar* or *Nymphaea*) were also present. The sampling locations will be situated between the upper and middle infralittoral zone and as close to the margin of emergent macrophytes as practical.

An Ekman grab sampler will be used to collect the surficial sediment samples. This sampler is best suited for use in soft, finely divided sediments. The Ekman grab sampler will not function well on sand substrates or at all where hard objects (e. g., sticks, leaves, stones, mollusc shells, etc.) are common. If sand substrates or hard objects are encountered the Ekman grab sampler may be modified by attaching a pole so that the sampler can be pushed into hard sediments in shallow water. Alternatively, if sand substrates or hard objects are encountered a Ponar grab sampler will be used. The Ponar grab sampler is well suited for sampling resistant sediments.

The Ekman or Ponar grab samplers will be cleaned between each sampling site. The sampler will be scrubbed with a dilute solution of MICRO (International Products Corp., Trenton, NJ) liquid laboratory cleaner followed by rinses with tap water, 10% nitric acid and finally distilled water. The waste solution used to rinse the grab sampler will be collected in a container and disposed with the waste solutions associated with the hydrogeologic investigation. The grab sampler will be wrapped in plastic until it is ready to be used. Immediately prior to use the grab sampler will rinsed in the water column above the sediment sampling location. Prior to the actual sample collection efforts will be made to prevent disturbing the sediments.

A randomly selected sampling location from Target Pond will be used to collect a field duplicate. Twice the normal volume of sediment will be collected and homogenized into a composite sample. Portions of the well-mixed composite sample will be transferred to the appropriate sample containers. This sample will be labelled as HMW-FBSD and submitted to the laboratory for chemical analysis. The location of the field duplicate will be recorded in the field notebook. A randomly selected sampling location from Target Pond will be used to collect a field blank. Following routine decontamination of the sediment grab sampler distilled water will be poured over the sampler. The water will be collected in a one-liter polyethylene bottle, preserved with nitric acid and submitted to the laboratory for chemical analysis of constituents

on the USEPA Target Analyte List (TAL). Water will also be collected in a one-liter polyethylene bottle, preserved with sulfuric acid and submitted to the laboratory for analysis of total organic carbon.

At each sampling location a surficial sediment sample (< 1 ft deep) will be collected. The texture and color of sediment at each sampling location will be described in the field notebook and photographically documented. The temperature of the sediment sample will also be recorded. The first two grab samples from each location will be placed inside of separate wide mouth sampling containers. Approximately 68 oz. (approximately 2 L) of sediment will be collected. These samples will be used by individuals at the University of Michigan to identify and enumerate the benthic macroinvertebrates. The benthic organisms will not be removed from the sediment during the field collection activities. The sediment containing the benthic macroinvertebrates will be placed on ice and returned to the University of Michigan the same day as collected. The contents of these samples will be washed through a no. 30 mesh sieve upon return to the laboratory. Subsequent grab samples will be placed inside of a polyethylene bucket. Approximately 192 oz. (approximately 5.7 L) of sediment will be collected. The subsamples will be gently homogenized with a plastic spoon until the texture and color appear uniform. Portions of the well-mixed composite sample will be transferred to the sample containers for the sediment toxicity evaluation (bioassay), chemical analysis, and geotechnical analysis. The specific sampling containers and preservation techniques are listed in revised Table 8-4 of the QAPP addendum (revised Section 8.0).

Samples for chemical analysis will be placed on ice in a cooler and delivered overnight by courier (Federal Express, Priority 1) at the end of each day to Enseco - Rocky Mountain Analytical Laboratory (Arvada, CO). The sample for the sediment toxicity evaluation will be placed on ice in a cooler and delivered at the end of each day by overnight courier (Federal Express Priority 1) to ABC Laboratories (Columbia, MO). The geotechnical samples will be

held until the conclusion of this phase of the field work and then submitted to MATECO Drilling Company (Grand Rapids, MI). The parametric coverage and laboratory standard operating procedures (SOPs) for the samples are listed in the addendum to the QAPP (revised Section 8.0). Chain of custody procedures will be followed for the collected and shipment of the samples.

2.8.2.2 Surface Water Samples

The sampling locations for the surface water samples will be the same as those used for the collection of sediment samples (revised Figure 2-5). The surface water samples will be collected before the sediment samples. In addition to collecting samples, vertical profiles of water temperature, specific conductivity, and dissolved oxygen will be completed.

To qualitatively analyze the phytoplankton community surface water samples will be collected with a 4-L Van Dorn water bottle. A composite over depth will be made and poured into a 1-L brown poly-bottle. The surface water samples for phytoplankton analysis will be placed on ice in a cooler and delivered by courier at the end of each day to the University of Michigan (Ann Arbor, MI). If the water is shallow at the sampling locations, the Van Dorn water bottle will not be used. Samples will be collected by immersing the 1-L brown poly-bottles approximately 6-inches below the water surface and allowed to fill with surface water. Once the poly-bottles are full they will be transferred to the cooler and subsequently delivered to the University of Michigan.

To qualitatively analyze the zooplankton community surface water samples will be collected by making several vertical hauls with a plankton net. The number of vertical hauls and length of the hauls necessary to collect a sufficient quantity of zooplankton will be recorded. The volume of sample collected will be large enough to provide a representative accounting of

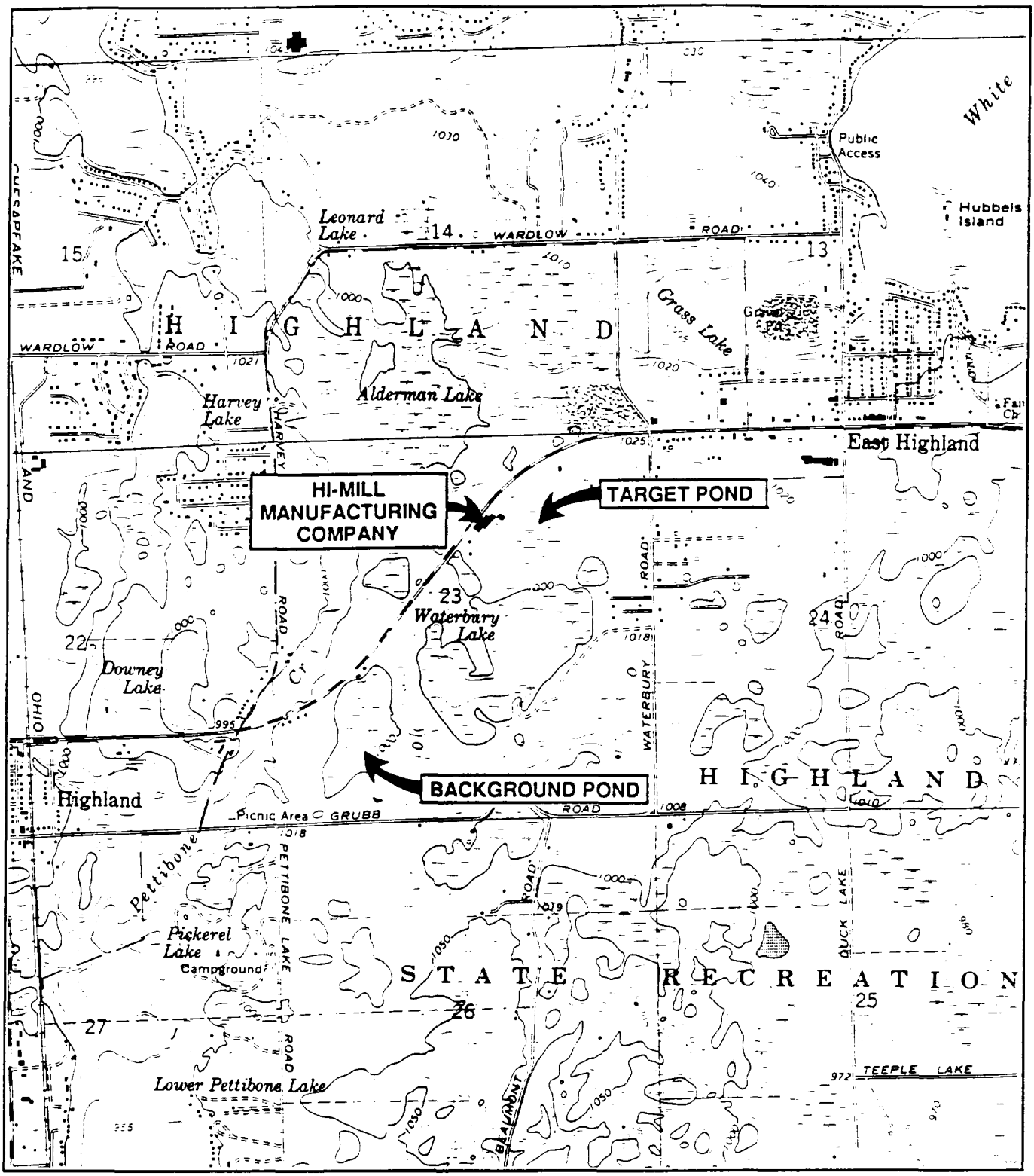
the taxa and numbers of individuals present at each sampling location. The plankton net will be constructed of no. 10 mesh and have a 0.5 m diameter opening. The net will be allowed to settle to the bottom before beginning the vertical haul. The contents of the net will be washed from the outside into a pint jar. Koechees solution (8% formalin in a saturated sugar solution) will be added in approximately equal volume to the retained volume of zooplankton in the jar. If the water is shallow at the sampling locations, the plankton net will not be initially used. Samples will be collected by immersing a wide-mouth 1-L poly-bottle approximately 6-inches below the water surface and allowing the bottle to fill. The water will then be poured through the plankton net and the retained zooplankton collected in a pint jar. The surface water samples for zooplankton analysis will be placed in a cooler and delivered by courier at the end of each day to the University of Michigan (Ann Arbor, MI).

The measurement of dissolved oxygen is one of the most frequently used and most important of all field measurements available for the investigation of the aquatic environment. Dissolved oxygen provides valuable information on the biological and chemical reactions in a waterbody. Specifically low dissolved oxygen levels could allow the mobilization of inorganic constituents from the sediment or threaten the fauna of Target Pond or Waterbury Lake with anoxia. To assist in determining if Target Pond or Waterbury Lake are thermally or chemically stratified water temperature and specific conductivity will be measured.

At each surface water and sediment sampling location a vertical profile of water temperature, specific conductivity, and dissolved oxygen will be recorded. In addition to these locations, a profile will be completed near the center of Target Pond and Waterbury Lake. A Yellow Springs Instrument Co. (YSI) Model 33 S-C-T Meter will be used to record specific conductivity and water temperature. The measured specific conductivity will be corrected to 25°C using values provided in Table 7-1 of Limnological Analyses (W.B. Saunders Co., Philadelphia). A YSI Model 57 Meter will be used to record the dissolved oxygen concentration. The percentage dissolved oxygen saturation for the recording taken immediately

below the water surface will be calculated using the water temperature and approximate altitude of the water surface. Correction factors for water temperature and altitude are provided in Tables I and II of the YSI Model 57 instruction manual. These field measurements will be recorded immediately below the water surface and at 0.5 m intervals until the bottom is reached. If the water column is shallow three measurements will be recorded; immediately below the water surface, at mid-depth, and immediately above the bottom.

832HIMILL/himill.sap



SOURCE: USGS 7.5 Minute Topographic Map, HIGHLAND, MICHIGAN Quadrangle 1983

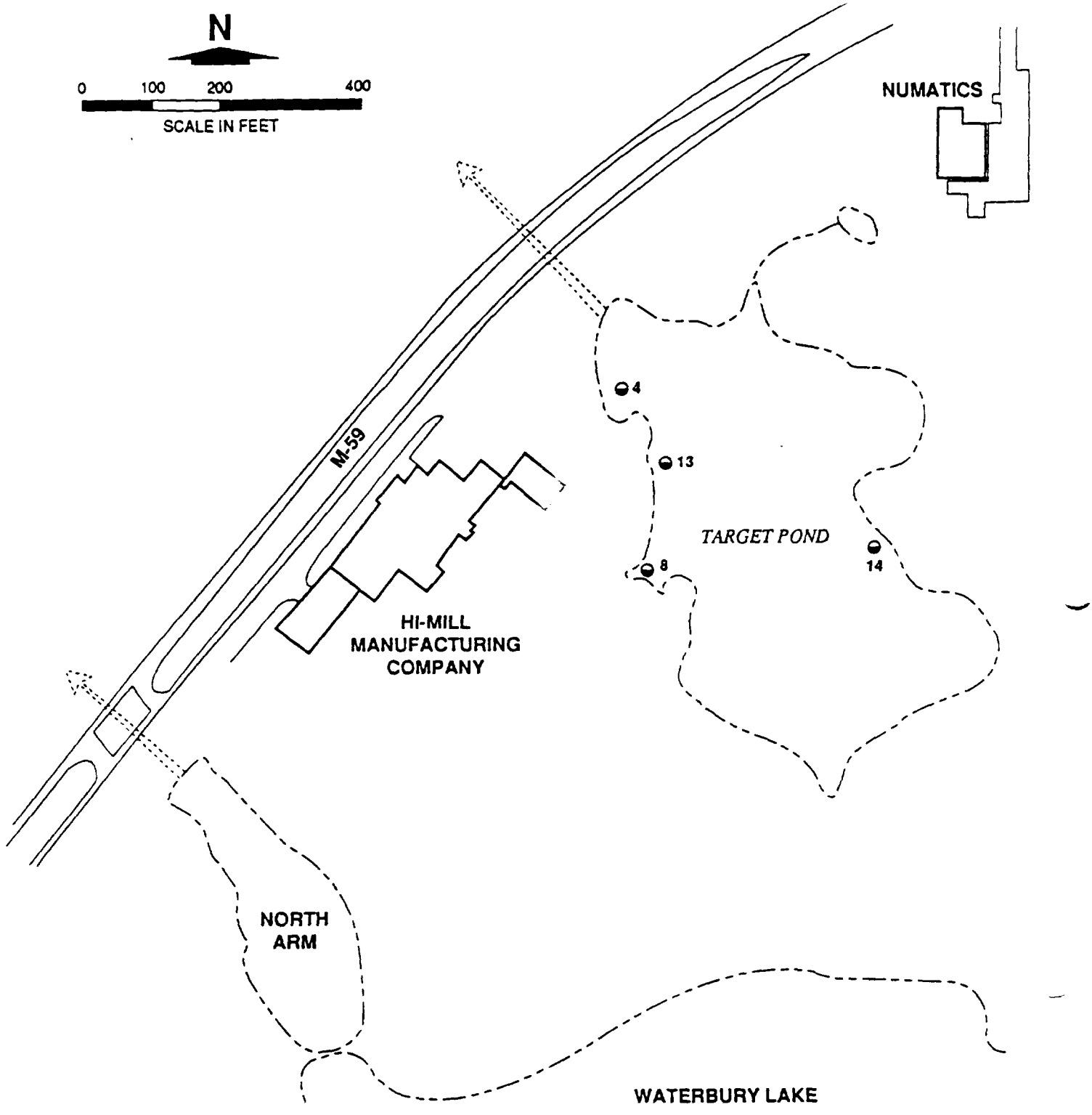
N

0 1000 2000 4000

SCALE IN FEET

GERAGHTY & MILLER, INC.
Environmental Services

FIGURE 2-1
SITE LOCATION MAP
HI-MILL MANUFACTURING COMPANY
HIGHLAND, MICHIGAN
MI135.04 - 0144.04



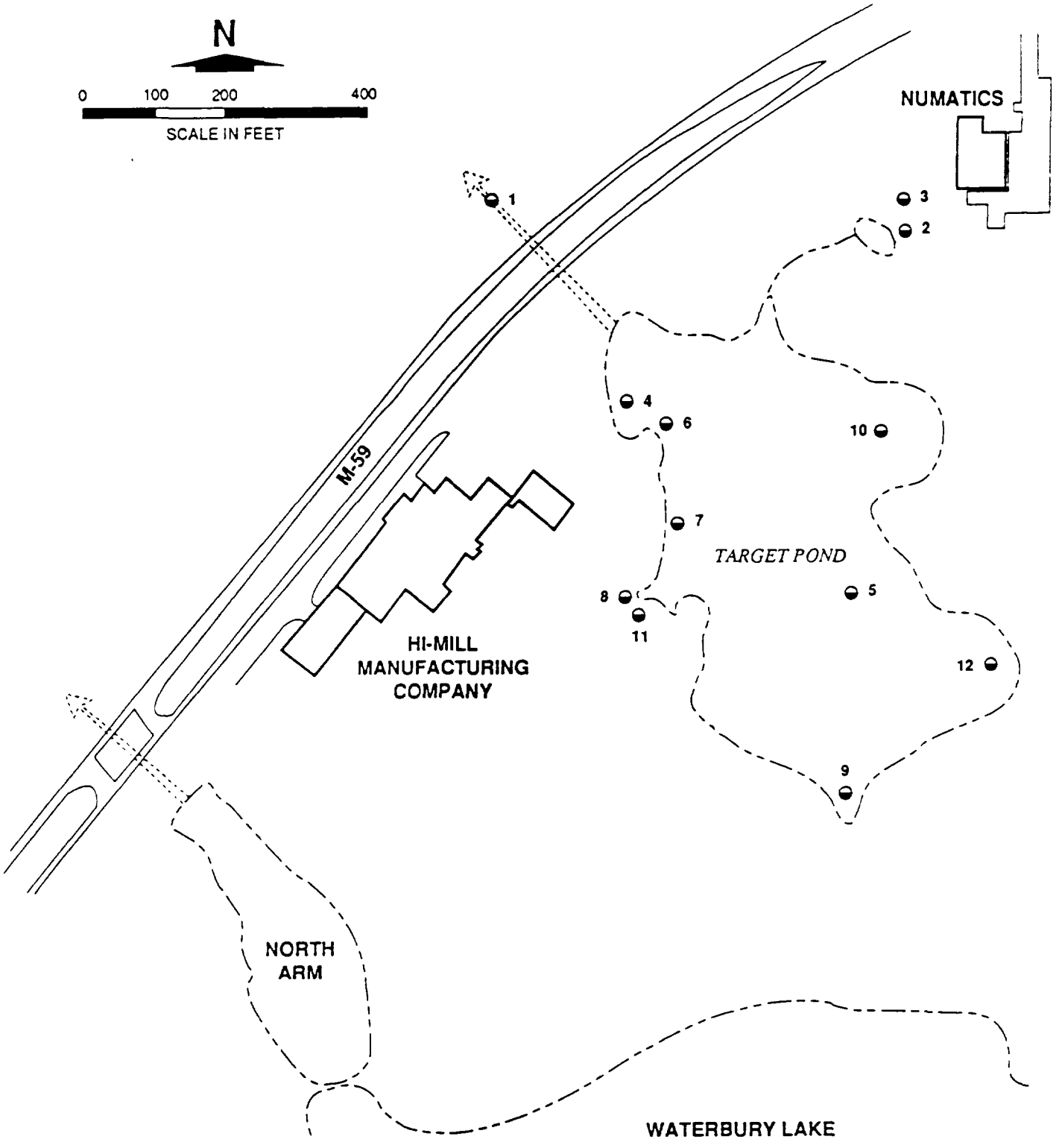
LEGEND

8 **SEDIMENT AND SURFACE WATER SAMPLING LOCATION**

NOTE : SAMPLE 15 AND 16 WILL BE COLLECTED FROM SOUTHERN PORTION OF WATERBURY LAKE

FIGURE 2-5
PROPOSED SEDIMENT AND SURFACE WATER SAMPLING LOCATIONS
HI-MILL MANUFACTURING COMPANY
HIGHLAND MICHIGAN
MI135.04 - 0144.05

GERAGHTY & MILLER, INC.
Environmental Services



LEGEND

● 1 SEDIMENT AND SURFACE WATER SAMPLING LOCATION

GERAGHTY & MILLER, INC.
Environmental Services

FIGURE 2-7
SEDIMENT AND SURFACE WATER SAMPLING LOCATIONS (FEBRUARY - MARCH 1990)
HI-MILL MANUFACTURING COMPANY
HIGHLAND MICHIGAN
MI135.04 - 0144.03

SECTION 8.0
QUALITY ASSURANCE PROJECT PLAN
ADDENDUM
REMEDIAL INVESTIGATION/FEASIBILITY STUDY
HI-MILL MANUFACTURING COMPANY
Highland, Michigan

Prepared by:

GERAGHTY & MILLER, INC.
126 N. Jefferson St.
Suite 400
Milwaukee, WI 53202

Approved by:

Project Coordinator	(Record Copy signed by Kevin Wolka)	
Geraghty & Miller, Inc.	**Kevin Wolka**	**Date**
Quality Assurance Officer	(Record Copy signed by Tim Davis)	
Geraghty & Miller, Inc.	**Tim Davis**	**Date**
Quality Assurance Officer	(Record Copy signed by Valerie Jones)	
USEPA Region V		**Date**
Remedial Project Coordinator	(Record Copy signed by Karla Johnson)	
USEPA Region V	**Karla Johnson**	**Date**

CONTENTS

APPENDICES

FIGURES

LIST OF TABLES

8.0 QUALITY ASSURANCE PROJECT PLAN

This revised Quality Assurance Project Plan (QAPP) was prepared as an addendum to collect sediment and surface water samples for subsequent laboratory analysis as part of the ecological inventory/assessment of Target Pond and Waterburg Lake. Information contained in this QAPP addendum amends the October 26, 1989 plan prepared by Techna Corporation (Plymouth, MI). The scope of this QAPP addendum was discussed by representatives of the U.S. Environmental Protection Agency (USEPA) and Geraghty & Miller during a pre-QAPP meeting on February 21, 1991. Appendix E contains the revised standard operating procedures provided by the USEPA on September 11, 1991.

8.1 Project Description

The project description as provided in the Quality assurance Project Plan (QAPP) dated October 26, 1989 is applicable except for the additional information which is to be inserted in sections 8.1.6 (Remedial Investigation Tasks), 8.1.8 (Intended Data Usage), and 8.1.9 (Project Schedule).

8.1.6 Remedial Investigation Tasks

The Remedial Investigation tasks related to the ecological inventory/assessment are presented in the attached work plan (Section 1.0). The principal activities of the ecological inventory/assessment include the following:

(1) A sediment toxicity evaluation (bioassay) using the test organisms *Hyalella azteca;*

(2) An ecological inventory of terrestrial and aquatic resources, and;

(3) A literature search.

The sediment toxicity evaluation will consist of collecting three sediment samples from Target Pond adjacent to the Hi-Mill Manufacturing Company and a fourth sediment sample from the east-central portion of Target Pond (see Figure 2-5 of the attached Sampling Plan). Previous results indicate that the highest concentrations of inorganic constituents are found in surficial sediment samples adjacent to the company. The fourth surficial sediment sample (TP14) from Target Pond will be collected from an area with relatively low concentrations of inorganic constituents. Two sediment samples will be collected from the southern portion of Waterburg Lake (see Figure 2-1 of the attached Sampling Plan). These two sediment samples from Waterburg Lake will represent an unimpacted control area. The six sediment samples will be submitted to the laboratory for analysis. The toxicity of the sediments will be evaluated using a 10-day static bioassay procedure. The survival and growth of the amphipod *Hyalella azteca* will be recorded. The concentration of the twenty-three inorganic constituents on the USEPA Target Analyte List (TAL) will be assessed in the sediment samples. The total organic carbon, pH, moisture content (percentage solids), and grain-size distribution will also be measured. These parameters may control the mobility and bio-availability of the inorganic constituents in the sediment samples. An examination of the relationship between sediment toxicity (if it exists) and concentrations of inorganic constituents in the sediment samples will be completed. If a predictable relationship exists, future delineation of toxicity sediments (if they exist) could be completed using chemical characterization of the sediments.

The ecological inventory of terrestrial resources will consist of a survey of the terrestrial biotic communities without sample collection. The objective is to obtain qualitative information on the biotic communities at the site, evaluate potential pathways by which biological receptors

could be exposed to contaminants, and determine whether any of the botic communities have been adversely impacted. Similar objectives apply to the aquatic inventory. To determine whether adverse ecological impacts have occurred in Target Pond samples of phytoplankton, zooplankton, and benthic macroinvertebrates will be collected. These samples will be collected from the sample locations used to collect the sediment samples. Upon receipt by the laboratory the different taxa in these communities will be identified and enumerated. At each sampling location and near the center of Target Pond and Waterbury Lake vertical profiles of water temperature, specific conductivity, and dissolved oxygen will be recorded.

The literature search will consist of accessing one or more databases to obtain information on the potential impacts of elevated levels of inorganic constituents on trees. Several trees near the Hi-Mill Manufacturing Company have died. Information obtained during the literature will be used to help evaluate whether the observed levels of inorganic constituents in soil and sediment samples from the site may have killed the trees.

8.1.8 Intended Data Usage

Data from the sediment toxicity evaluation will be used to help determine if the sediment in Target Pond is toxic to benthic macroinvertebrates. The qualitative inventory of benthic macroinvertebrates will also be used to help determine if changes have occurred in the composition or numbers of benthic organisms at the sampling locations in Target Pond. A determination of toxic impacts to the overlying water column will be assessed by qualitatively evaluating the composition and number of phytoplankton and zooplankton. The chemical analysis of the sediment "samples will be used to provide(d) additional qualitative information on the levels and extent of organic contamination in target pond only."[1] Field measurements

[1] Changes provided by the USEPA, Quality Assurance Section; September 11, 1991.

of dissolved oxygen will provide information on the potential mobilization of inorganic constituents from the sediment and the threat of anoxia to the aquatic fauna. Specific conductivity and water temperature will assist in determining if the water-bodies are chemically or thermally stratified.

The results from Target Pond will be compared to background (control) samples collected from nearby Waterbury Lake. This will include the sediment toxicity evaluation, qualitative benthic macroinvertebrate, phytoplankton, and zooplankton inventory, chemical and geotechnical analysis of the sediments and field measurements of water temperature, specific conductivity and dissolved oxygen.

Information generated during the ecological inventory/assessment will be included in the RI report which is scheduled to be completed in September or October 1991. This information will help to define the nature and extent of contamination at the site. Actual and potential adverse ecological impacts associated with contaminants at the site will also be included in the RI report. Components of the ecological inventory/assessment will be used to address important exposure pathways and environmental receptors at the site. This material will be incorporated in the Baseline Risk Assessment. Aspects of the ecological inventory/assessment will be included during the screening of potential remedies for the site.

8.1.9 Project Schedule

A bar chart consisting of the tasks for the ecological inventory/assessment and the time lines is presented as revised Figure 8-4. The completion of this project schedule assumes that the revised project plans for the ecological inventory/assessment are approved by the U.S. Environmental Protection Agency (USEPA) and the Michigan Department of Natural Resources (MDNR) on or before June 28, 1991.

8.2 Project Organization

The project organization of the October 26, 1989 QAPP is applicable except for several changes. Techna Corporation (Plymouth, MI) developed and submitted the initial set of project plans. These plans were subsequently approved by the USEPA and MDNR. Techna Corporation conducted the field work described in the plans and submitted to the USEPA and MDNR a draft copy of the Remedial Investigation (RI) report on June 21, 1990. Geraghty & Miller was then retained by Hi-Mill Manufacturing Company and will be completing the additional hydrogeologic and ecologic inventory/assessment. The project organization was modified and is shown schematically in revised Figure 8-5.

The following revised responsibilities for key personnel associated with the ecological inventory/assessment are described below:

Project Officer [2]

Ed Rothschild (Geraghty & Miller) will serve as the project officer for the Hi-Mill RI/Feasibility Study (FS). Mr. Rothschild will have final responsibility for the technical quality of the project. The project officer has the corporate authority to retain subcontractors necessary to complete the field work and/or preparation of the RI report and FS.

Project Coordinator

Kevin Wolka, P.E., Ph.D. (Geraghty & Miller) will serve as the project coordinator for the Hi-Mill RI/FS. Dr. Wolka will have overall technical, quality, and resource management

---

[2] Project Officer was changed from Keith Flemingloss to Ed Rothschild

responsibility for the project. He will ensure that the project is performed in accordance with the project plans and schedule. The project coordinator will also document and approve any deviations from the approved project plans.

QA/QC Officer

Tim Davis (Geraghty & Miller) will serve as the quality assurance/quality control (QA/QC) officer for the Hi-Mill RI/FS. Mr. Davis will be responsible for any changes in sampling protocols, corrective actions, and deviations in quality control. He will also be responsible for ensuring that appropriate QA/QC audits and system reviews are performed during the sampling and chemical analysis phase of the RI and that all sampling and analysis QA/QC data is reviewed with respect to the QA/QC objectives. Mr. Davis will be responsible for the final data review, the review of tentatively identified compounds (TICs), and the review of the special analytical services (i.e., bioassay and aquatic inventory). He will be assisted by Mr. Dale Scherger (ENCOTEC, Ann Arbor, MI), Dr. Peter Meier (University of Michigan, Ann Arbor, MI), Mr. Steve Elliot (MATECO Drilling Company, Grand Rapids, MI), and Ms. Dorothy England (ABC Laboratories, Columbia, MO).

Ecological Inventory/Assessment

Steve Ellingson (Geraghty & Miller) will be responsible for the field work, data interpretation and report preparation for the aquatic inventory/assessment and Todd Udvig (Geraghty & Miller) will perform a similar function for the terrestrial inventory/assessment. Messrs. Ellingson and Udvig will be assisted by other Geraghty & Miller staff during field sampling and measurements.

Dr. Peter Meier (University of Michigan, Ann Arbor, MI) will be responsible for completing the aquatic inventory. This will include identification and enumeration of phytoplankton, zooplankton, and benthic macroinvertebrates.

Ms. Dorothy England (ABC Laboratories, Columbia, MO) will be responsible for conducting the sediment toxicity evaluation. This will include a 10-day static bioassay procedure for determining the toxicity of sediment using *Hyalella azteca*. Ms. England will be assisted by the Quality Assurance Unit of ABC Laboratories.

Risk Assessment

In accordance with recent policy changes by the USEPA the risk assessment will be completed by the USEPA. Geraghty & Miller will provide risk assessment information to the USEPA and will support the USEPA as appropriate to complete this task. Dr. Frank Jones (Geraghty & Miller) will serve to support the risk assessment for the Hi-Mill RI/FS. He will be responsible for coordinating the collection and initial evaluation of data for the risk assessment. This information will be submitted to the USEPA.

Feasibility Study

The FS responsibilities will be assumed by Greg Vanderlaan. He will be responsible for coordinating the data collection and evaluation activities of the FS team and for reviewing the results and conclusions of the FS.

Subcontractors [3]

Steven J. Wright, Ph.D. (University of Michigan, Ann Arbor, MI) will no longer be retained as the consulting hydrogeologist. McDowell and Associates, Inc. (Ferndale, MI) will no longer be retained for soil boring and monitoring well installation or geotechnical analyses. Encotec (Ann Arbor, MI) will no longer be retained for the chemical analyses.

The following three subcontractors will be added to the project team:

Aquatic Inventory

Peter G. Meier, Ph.D.
Professor of Environmental Health
School of Public Health
Department of Environmental and Industrial Health
The University of Michigan
Ann Arbor, Michigan 48109-2029
(313) 936-0737 FAX (313) 764-9424

Sediment Toxicity Evaluation (Bioassay)

Dorothy England
ABC Laboratories
7200 East ABC Lane
Columbia, Missouri 65205
(314) 474-8579 FAX (314) 443-9033

---

[3] Chemical analyses will not be completed by Encotec, but rather Enseco - Rocky Mountain Analytical Laboratory.

Drilling and Geotechnical Analyses

Steve Elliot
MATECO Drilling Company
693 Plymouth Avenue NE
Grand Rapids, Michigan 49505
(616) 459-1090 Fax (616) 456-5784

Chemical Analyses

Brian Patlen
Enseco - Rocky Mountain Analytical Laboratory
4955 Yarrow Street
Arvada, Colorado 80002
(303) 421-6611 Fax (303) 431-7171

8.3 Quality Assurance Objectives for Measurement Data

The quality assurance objectives as stated in the October 26, 1989 QAPP are applicable except for the following modifications and clarifications to the introduction of section 8.3, 8.3.3 (Data Representativeness), Table 8-1 (Organic and Inorganic Method Audits), Table 8-1A (Levels of Data Quality Objectives), and Table 8-2 (Inorganic Target Analyte List).

This modification to the introductory sentence in section 8.3 shall be made:

The quality assurance objectives described below are designed to ensure that the chemical and ecological data generated during the Hi-Mill RI meet the goals of the RI, are suitable for use in the FS and are usable for any future enforcement action.

8.3.3 Data Representativeness

Sampling locations have been chosen so that the results of chemical and ecological analyses of the collected samples will provide sufficient data to determine the following:

- the extent of adverse ecological impacts to aquatic and terrestrial communities adjacent to the Hi-Mill Manufacturing Company

- the extent of sediment toxic to benthic macroinvertebrates

To complete the ecological inventory/assessment several additional laboratory parameters will be measured. These will include total organic carbon, pH, moisture content (total solids), and grain size distribution. An inventory of benthic macroinvertebrates, phytoplankton, and zooplankton will also be completed. This information on sample matrix, field measurements, laboratory parameters, and levels of data quality objectives (DQOs) was initially provided in Table 8-1A and Table 8-3 of the October 26, 1989 QAPP. The aforementioned information to support the ecological inventory/assessment will consolidated into a revised Table 8-1A. The DQOs for field and laboratory measurements of each sample matrix will be combined with the proposed number of investigative samples, field duplicates, field blanks, matrix spike samples, and spike duplicate samples.

Method audits will be conducted during the completion of the sediment toxicity evaluation. A revised Table 8-1 provides information on the audits and control limits. A negative control will consist of ten *Hyalella azteca* added to beakers containing contaminant-free control sediment provided by ABC Laboratories. The negative control will be run in parallel with the investigative samples. The final test results will be deemed in control if at least 90% of the *Hyalella azteca* survive in the negative controls. A positive control will consist of adding a reference toxicant to the lot of *Hyalella azteca* used to run this sediment toxicity evaluation. The reference toxicant will be supplied by the USEPA and will consist of sodium dodecyl

sulfate. The test results will be deemed in control of all of the *Hyalella azteca* are killed within 48 hours after the reference toxicant is added.

Table 8-2 (Inorganic Target Analyte List) is revised to include 23 inorganic constituents (aluminum through zinc). The sediment samples will not be analyzed for levels of cyanide, hexavalent chromium, ammonia, or nitrate plus nitrite.

8.4 Sampling Procedures

The procedures and methodologies that will be used for the collection of samples during the ecological inventory/assessment are described in detail in revised Section 2.0 (Remedial Investigation Sampling Plan). Specific sampling techniques that will be used for each sample matrix are referenced as follows:

- Surface waters and sediments - Revised Section 2.8

A summary of the samples that will be collected and the related chemical analysis parameters is presented in revised Table 8-1A. Descriptions of the sample bottles that will be used and the holding times that will be observed for each sample type are presented in revised Table 8-4.

8.5 Chemical Analysis Procedures [4]

The chemical analysis procedures provided in the October 26, 1989 QAPP are applicable except for the following revision and addition:

---

[4] Chemical analyses will not be completed by Encotec, but rather Enseco - Rocky Mountain Analytical Laboratory.

A summary of sample matrices, preservation techniques, holding times, and containers for the ecological inventory/assessment is presented in revised Table 8-4.

A number of non-Contract Laboratory Program (CLP) analytical procedures will be used during the completion of the ecological inventory/assessment. A copy of the standard operating procedures (SOPs) for the non-CLP methods is provided in revised Appendix B. The following non-CLP SOPs will be used:

(1) Sediment toxicity evaluation (bioassay) (ABC Laboratory SOP No. 9007);

(2) Identification and enumeration of phytoplankton, zooplankton, and benthic macroinvertebrates (University of Michigan);

(3) Total organic carbon, pH, and moisture content (percentage solids)(Enseco - Rocky Mountain Analytical Laboratory), and;

(4) Grain-size distribution by mechanical sieving and hydrometer [ASTM D 422-63 (reapproved 1972)].

8.6 Sample Custody

The sample custody procedures described in the October 26, 1989 QAPP are applicable except for the following clarification and change in the location of the final evidence file:

A chain-of-custody (COC) form similar to that presented as Figure 8-6 will be used during the ecological inventory/assessment. Geraghty & Miller COC forms (form no. G&M09 12/88) will be utilized.

8.6.3 Final Evidence File

The final evidence file will be stored in a secure, limited access area in the Detroit office of Geraghty & Miller.

8.7 Calibration Procedures and Frequencies

The calibration procedures and frequencies presented in the October 26, 1989 QAPP are applicable as presented. Additional information on the calibration of the TOC analyzer is presented in the attached SOP (revised Appendix B).

8.8 Data Reduction, Validation and Reporting [5]

The data reduction, validation, and reporting procedures presented in the October 26, 1989 QAPP are applicable except for the following addition:

Initial data reduction, validation, and reporting responsibilities for laboratory data lie with Enseco - Rocky Mountain Analytical Laboratory (Arvada, CO), MATECO Drilling Company (Grand Rapids, MI), ABC Laboratories (Columbia, MO), and the University of Michigan (Ann Arbor, MI).

8.9 Internal Quality Control Procedures

The internal quality control procedures described in the October 26, 1989 QAPP are applicable except for the following addition:

---

[5] Chemical analyses will not be completed by Encotec, but rather Enseco - Rocky Mountain Analytical Laboratory.

Internal quality control requirements for the analysis of total organic carbon, pH, moisture content, and the sediment toxicity evaluation are specified in the attached SOPs (revised Appendix B).

8.10 Performance and System Audits

The performance and system audits described in the October 26, 1989 QAPP are applicable except for the following revision:

The project coordinator (Kevin Wolka, Geraghty & Miller) or QA/QC officer (Tim Davis, Geraghty & Miller) will be responsible for auditing the field team to ensure compliance with the operating procedures, sample custody, and QA/QC requirements. Because the scope and duration of the ecological inventory/assessment is relatively limited, compared to the previous hydrogeologic investigation, a full scale audit will not be conducted. Spot check audits of specific procedures may be performed.

8.11 Preventative Maintenance

The section on preventative maintenance in the October 26, 1989 QAPP is applicable as presented. Additional information of the preventative maintenance of the TOC analyzer is provided in the attached SOP (revised Appendix B).

8.12 Specific Routine Procedures Used to Assess Data Precision, Accuracy, and Completeness

The section on specific routine procedures used to assess data precision accuracy and completeness in the October 26, 1989 QAPP is applicable as presented except that a Geraghty & Miller QA officer will assess the data.

8.13 Corrective Action

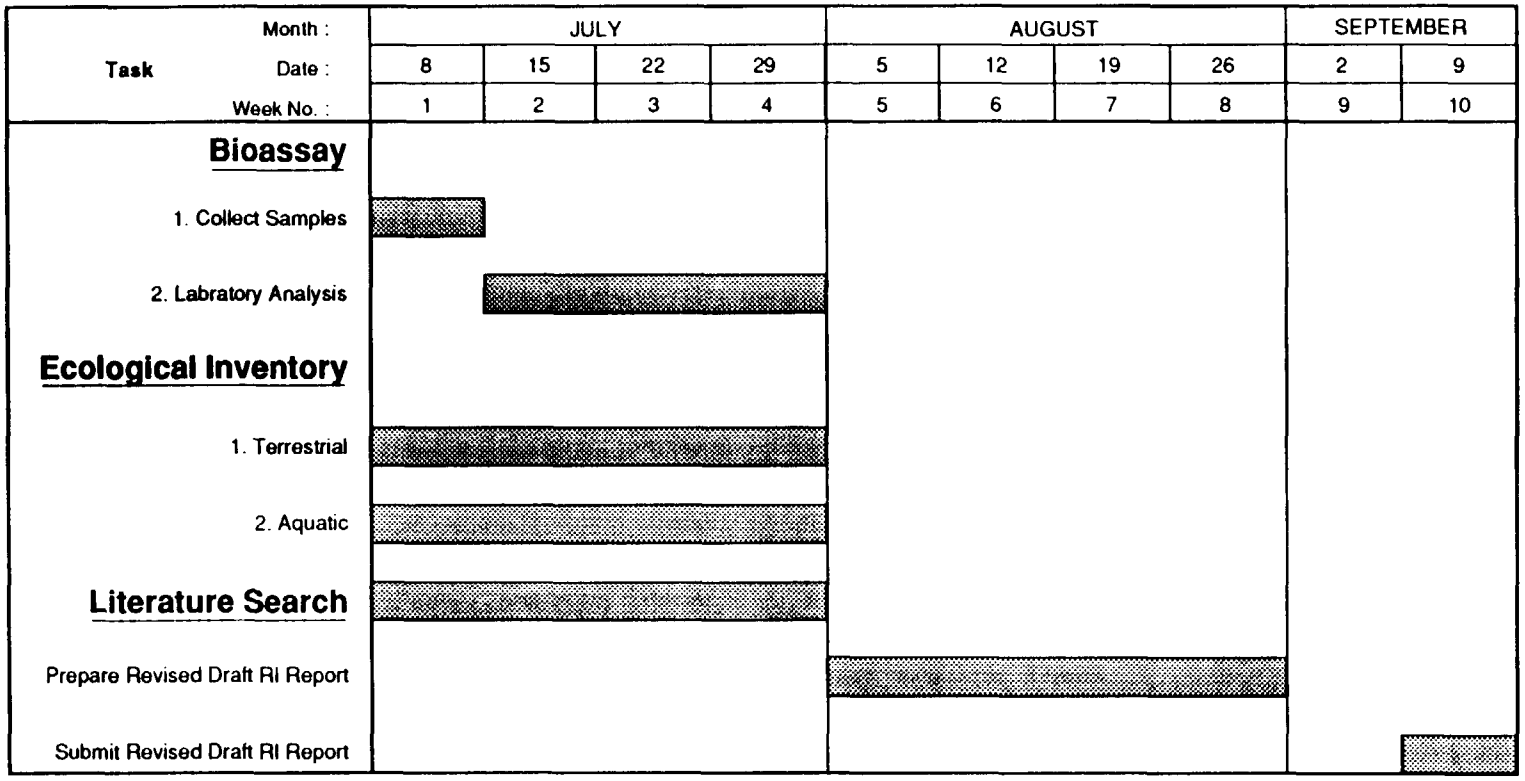
The corrective action described in the October 26, 1989 QAPP is applicable except for the following modification:

Corrective actions for laboratory analyses will be implemented through consultations between the Geraghty & Miller QA/QC officer (Tim Davis) and the respective laboratory QA/QC officers. The Geraghty & Miller project coordinator (Kevin Wolka) will make immediate decisions on new protocols to be implemented after consultation with the Geraghty & Miller QA/QC officer. Specific corrective actions for the sediment toxicity evaluation are provided in the attached SOP (revised Appendix B).

8.14 Quality Assurance Reports to Management

The discussion of quality assurance reports to management are presented in the October 26, 1989 QAPP is applicable as presented.

832HIMILL/qapp.add



NOTE : Assumes that project plans are approved on or before June 28, 1991.

FIGURE 8-4
(REVISED JUNE 1991)
PROJECT SCHEDULE FOR THE ECOLOGICAL INVENTORY ASSESSMENT
HI-MILL MANUFACTURING COMPANY
HIGHLAND, MICHIGAN
MI135.04 - 0144 06

GERAGHTY & MILLER, INC.
Environmental Services

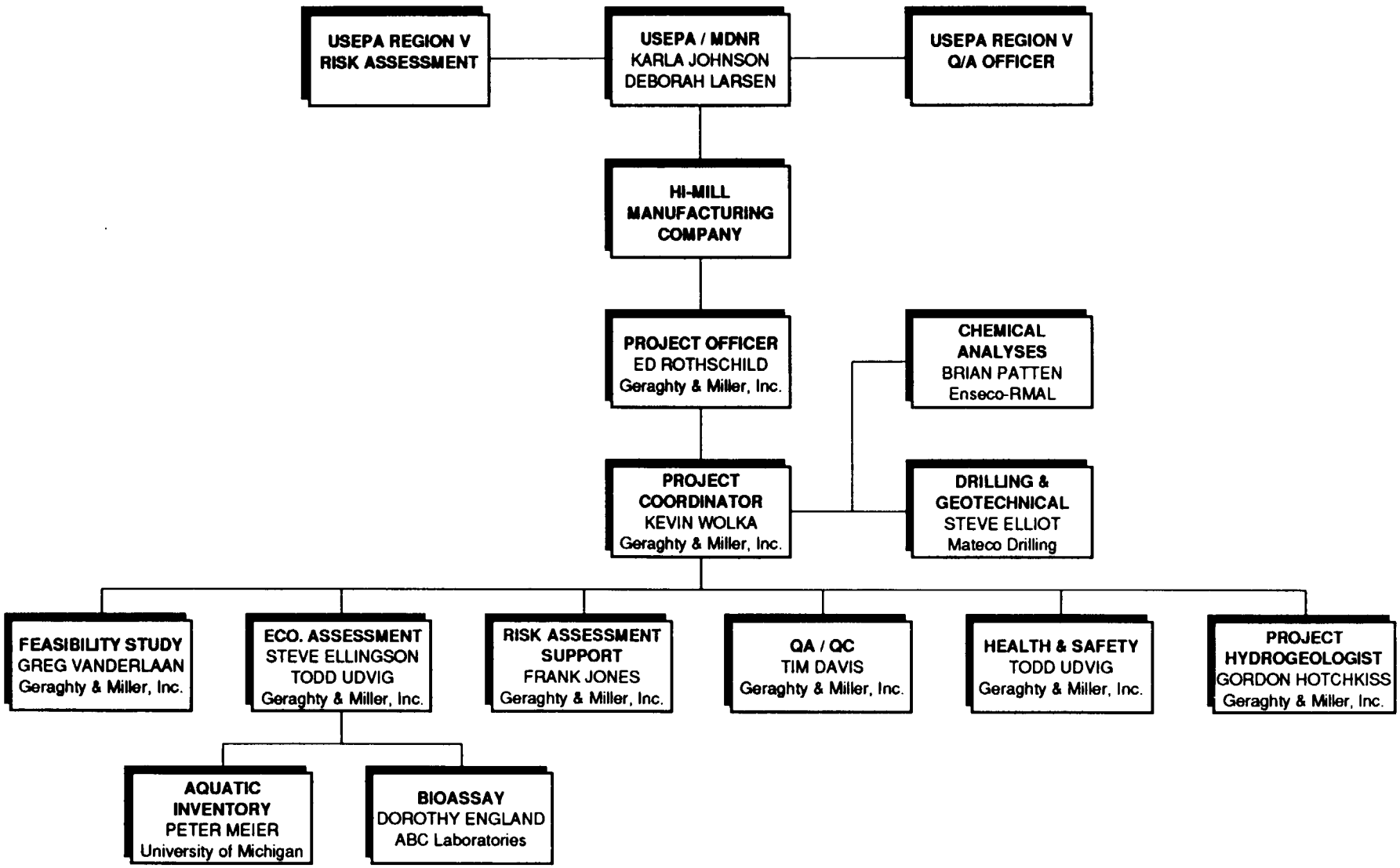


FIGURE 8-5
(REVISED SEPTEMBER 1991)
PROJECT ORGANIZATION CHART
HI-MILL MANUFACTURING COMPANY
HIGHLAND, MICHIGAN
MI135.04 - 0144.01

GERAGHTY & MILLER, INC.
Environmental Services

TABLES

Table 8-1. Ecological Inventory/Assessment Method Audits (Revised March 1991).

Parameter	Audit	Control Limits
Sediment Toxicity (Bioassay)	Negative Control	>90% survival in controls
	Positive Control	100% mortality within 48 hours using reference toxicant
Total Organic Carbon(a)	Matrix Duplicate	Relative percentage difference ≤30%
pH	Matrix Duplicate	Relative percentage difference ≤30%
Moisture Content (Total Solids)	Preparation Blank	Percentage total solids 0%
	Matrix Duplicate	Relative percentage difference ≤30%

(a) - Accuracy and precision will conform to the limits in the September 11, 1991 letter from the USEPA, Quality Assurance Section.

832HIMILL/eccmnd.wk1

Table 8-1A. Summary of Sampling and Analysis Program, Hi-Mill Manufacturing Company, Highland, Michigan (Revised March 1991).

Sample Matrix	Field (a) Measurements	Laboratory Parameters	DQO Analytical Level	Investigative Sample			Field Duplicate			Field Blank			MS/SD			Matrix Total
				No.	Freq.	Total	No.	Freq.	Total	No.	Freq.	Total	No.	Freq.	Total	
Sediment	Temperature	CLP RAS Inorganics Metals	IV	6	1	6	1	1	1	1	1	1	0	0	0	8
		Bioassay	V	6	1	6	0	0	0	0	0	0	0	0	0	6
		TOC, pH, Moisture Content	V	6	1	6	1	1	1	1	1	1	0	0	0	8
		Grain-size Distribution	III	6	1	6	0	0	0	0	0	0	0	0	0	6
		Benthic Macroin-vertebrates	V	6	1	6	6	1	6	0	0	0	0	0	0	12
Surface Water	Temperature	Phyto-plankton	V	6	1	6	0	0	0	0	0	0	0	0	0	6
	Water Depth	Zoo-plankton	V	6	1	6	0	0	0	0	0	0	0	0	0	6

a = DQO Analytical Level for field measurements is I.

HIMILL/sumana.wk1

Table 8-2. Inorganic Target Analyte List (TAL) (Revised June 1991).

Inorganics	Method	Soil/ Sediment mg/kg
Aluminum	200.1	40
Antimony	204.2	12
Arsenic	206.2	2
Barium	200.1	40
Beryllium	200.1	1
Cadmium	200.1	1
Calcium	200.1	1000
Chromium	200.1	2
Cobalt	200.1	10
Copper	200.1	5
Iron	200.1	20
Lead	239.2	0.6
Magnesium	200.1	1000
Manganese	200.1	3
Mercury	245.1/245.5	0.1
Nickel	200.1	8
Potassium	200.1	1000
Selenium	270.2	1
Silver	200.1	2
Sodium	200.1	1000
Thallium	279.2	2
Vanadium	200.1	10
Zinc	200.1	4

Note: Due to unforeseeable circumstances some samples may be analyzed by a different method as long as the limits are met.

832HI-MILL/intarget.wk1

Table 8-4. Sample Containers and Preservatives for the Ecological Investory/Assessment (Revised March 1991).

Parameter	Container	Preservation	Holding Time
Sediment			
Metals	Wide Mouth Glass (8 oz; 3/4 full)	Cool 4°C	180 days except mercury 26 days
Bioassay	Wide Mouth HDPE (128 oz; 3/4 full)	Cool 4°C	14 days
TOC, pH, moisture content	Wide Mouth Glass (8 oz; 3/4 full)	Cool 4°C	28 days, 24 hours, and 7 days, respectively
Grain size distribution	Plastic Bag (32 oz; 1/4 full)	None	Not applicable
Benthic Maro-invertebrates	Wide Mouth HDPE (16 oz; 3/4 full)	Cool 4°C and 90% ethanol (a)	Not established, analyze as soon as practical
Surface Water			
Phytoplankton	Brown Polybottle (32 oz; 3/4 full)	Cool 4°C and/or 5 ml Lugol's Solution (b)	Not established, analyze as soon as practical
Zooplankton	Wide Mouth HDPE (8 oz; 3/4 full)	Koechees solution (c)	Not established, analyze as soon as practical

a = Once the field sample is returned to the laboratory it will be washed through a No. 30 sieve and the retained portion will be preserved with 90% ethanol.

b = If the sample is not analyzed immediately upon return to the laboratory, it will be preserved with 5 mL of Lugol's solution which consists of 60 g potassium iodide and 60 g iodine crystals in 1000 mL of distilled water.

c = The contents of the net will be washed into the container and an equal volume of Koechees solution (8% formalin in a saturated sugar solution) will be added to the container.

Note: Holding times are from date of sample collection.

APPENDIX B

ABC PROTOCOL NO. 9007

(Prepared for Geraghty & Miller, March 12, 1991)

10-Day Static Bioassay Procedure for Determining the Toxicity of Xenobiotic Sediment Contaminants to *Hyalella azteca*

ABC laboratories' Study Number _____

Test Material _____

This protocol complies with testing procedures described in ASTM Document #1 E 1383.

1.0 INTRODUCTION

Aquatic toxicity tests have been used extensively in the assessment of the environmental effects of chemical substances. Indeed, aquatic bioassays are required by federal laws such as the Toxic Substances Control Act (TSCA) (1), Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) (2), and the Clean Water Act of 1977 (3). Testing guidelines have been presented for determining the acute toxicity of pesticides regulated by FIFRA (4) and other chemical substances which fall under the jurisdiction of TSCA (5). While these tests have stressed the concentrations of test chemical in the water column, such experiments rarely reflect the dynamic systems that exist in nature. Only recently has attention been given to sediment quality and the influence of xenobiotic-laden sediments on benthic invertebrates. Adverse effects of contaminated sediments on aquatic biota have been documented (6, 7), and recent ASTM guidelines have been developed for testing sediment toxicity (15). It is the intent of this protocol to provide a methodology to assess the toxicity of contaminated natural sediments to a representative aquatic invertebrate, *Hyalella azteca*.

Analytical Bio-Chemistry Laboratories, Inc. (ABC Laboratories) has prepared the following protocol to comply with FIFRA (40 CFR 160) testing guidelines, ASTM sediment testing criteria (subcommittee E47.03 Documents E 1383 and E 1391) and the Good Laboratory Practice regulations (8).

2.0 OBJECTIVES

The primary objective of the toxicity test described herein is to evaluate the toxicity of one or more field-collected sediments to *Hyalella azteca* under static conditions. This is achieved with a 10-day partial life cycle exposure to the sediment. Toxicity is evaluated in light of 10-day survival and growth (live biomass) of the aquatic amphipod, *Hyalella azteca*.

3.0 TESTING FACILITY

The study will be conducted by the Aquatic Toxicology Division of Analytical Bio-Chemistry Laboratories, Inc., 7200 East ABC Lane, P.O. Box 1097, Columbia, Missouri, 65205, 314-474-8579.

4.0 METHODS AND MATERIALS

4.1 General. The bioassay method presented here was patterned after procedures described by Adams, et. al. (6), the American Society for Testing and Materials (9, 15), and the U.S. Environmental Protection Agency (10, 11).

4.2 Test Organisms.

4.2.1 Source and Justification. The test lot of amphipods will be provided by an ABC Laboratories' in-house culture. This culture was obtained from the National Fisheries Contaminant Research Center (NRCRC, USDI-FWS) in Columbia, Missouri on February 27,1990. The original NFCRC culture was obtained in August of 1986 from Alan Nebeker, Ph.D., U.S. EPA, Corvallis, Oregon. The species of choice will be *Hyalella azteca*, rather than *Gammarus fasciatu, G. pseudolimnaeos* or *G. leoustris*. *H. azteca* is easier to culture and does not exhibit the cannibalistic tendencies of the *Gammarus* species (12). More importantly, it has been shown to exhibit toxicity responses similar to those of *Gammarus* species and to daphnids (13, 14), and is a recommended species in ASTM guidelines (15).

4.2.2 Culture and Acclimation to Test Conditions. All test organisms will be held in a controlled-temperature area on a 16-hour daylight photoperiod (light intensity 70-100 foot candles) at the same temperature used for testing (20 ±2°C). The *Hyalella azteca* will be cultured in aged, hard-maple leaves and fed a suspension of fish starter mash, yeast, cereal leaves, alfalfa pellets and algae once weekly.

Testing will be carried out using juveniles of the same age and size. Acclimation will be performed by transferring 3- to 5-day old juveniles to a 50:50 dilution of well water and test water. After 2 to 3 hours, the organisms will be transferred to a dilution of 25% well water and 75% test water. After an additional 2 to 3 hours, the *Hyalella azteca* will be placed in 100% test water. Gradual temperature acclimation will be accomplished by a 2-3°C adjustment per day until test temperature is reached.

4.2.3 Reference Toxicants. Representative apmhipods from the ABC in-house culture will be tested with a reference toxicant supplied by the USEPA. The reference toxicant used in this test will be a solution of sodium dodecyl sulfate (SDS), otherwise designated as Reference Toxicant #1. As no reference toxicity data is currently available for this test species, a range-finding test will be performed to establish an approximate range of toxicity. From this data a definitive 96-hour static acute test will be performed to determine an approximate LC_{50} for the amphipods.

Following the LC_{50} determination and prior to or concurrent with the sediment exposure, the lot of amphipods to be used in this sediment test will be exposed to a known lethal level of reference toxicant, as established by the LC_{50} test. Ten juvenile *Hyalella azteca* (2-3 mm) will be placed in one- to two-liter glass beakers containing approximately 200 ml of negative contaminant-free

control sediment supplied by ABC Laboratories and 800 ml of test water. The reference toxicant will be added to the glass beakers and stirred, followed by addition of the test organisms within 30 minutes. The beakers will be observed for mortality and behavioral abnormalities at 24 and 48 hours. The test will be deemed acceptable of 100% of the amphipods die within 48 hours.

4.3 Test System. The test will be conducted in one- or two-liter glass beakers containing approximately 200 ml of sediment and 800 ml of test water. These test vessels will be placed in a temperature-controlled water bath with temperature maintained at 20 ± 2°C. A continuous record of the test area temperature will be maintained and presented in the raw data appendix to the toxicity test report. The test will be conducted ona 16-hour daylight photoperiod at a light intensity of 70-100 foot candles. The dilution water used in toxicity testing at ABC Laboratories will be ABC Laboratories well water prepared to a total hardness of between 160 to 180 mg/L (as $CaCO_3$). The specific water hardness will be achieved by blending naturally hard ABC Laboratories well water with ABC Laboratories well water that has been demineralized by reverse osmosis (RO).

4.4 Test Material. Specific information regarding the test sediment is to be supplied by the sponsor and will be addressed at the time of protocol approval in section 9.3. Sediment collection and shipment shall be the responsibility of the study sponsor, and should follow guidelines set forth in ASTM Document #3 E 1391 (16).

Three different sediments will be tested. These will include four samples of impacted sediments, two background samples of unimpacted sediments and a negative contaminant-free control sediment, which will be supplied by ABC Laboratories.

4.5 Test Procedure.

4.5.1 General. Sediments collected from field sites will be screened through an appropriately-sized sieve to remove indigenous organisms and large particles of debris, or forceps may be used if sieving is not appropriate. Passing the sediment through an appropriately-sized sieve and removing indigenous organisms will eliminate interferences due to predation by the indigenous organisms. Sieving should be done just prior to preparation of test chambers, each of which will receive approximately 200 ml each of either test or control

sediment (the exact weight or volume will be recorded). The sediment will be leveled with a spatula, if necessary, and 800 ml of test water will be added by slow introduction down the side of the beaker. The sediment/water preparation will be placed in a temperature- controlled water bath and allowed to equilibrate for 12 to 24 hours prior to test initiation.

4.5.2 Biological. Test organisms will be selected from a sub-culture of 2nd to 3rd instar individuals (2-3mm). The subculture will consist of *Hyalella azteca* hatched in hard water culture and acclimated gradually to test dilution water. *Hyalella azteca* will be maintained within the test temperature range for at least 48 hours prior to testing. Test organisms will be fed at least three times weekly prior to test initiation, a suspension of the same food used in culture.

The test will be conducted using three or four replicates for each impacted sample and each background sample. Three or four replicates of the control sediment will also be used. The definitive test will be initiated by impartial, random addition of test organisms 12 to 24 hours after preparation of the test system. This will be accomplished by sequentially adding one organism per test chamber until all test chambers contain their complement of 10 *Hyalella azteca*. Alternately, the test organisms may be distributed impartially to holding beakers prior to addition to test chambers.

Test organisms will be fed three times weekly 1.0 ml of food suspension prepared at a concentration of 5.0 mg/ml suspended solids. A record of food preparation and feeding will be maintained during the test. The test chambers will be observed for mortality and/or adverse behavioral effects at 10 days. A record will be maintained of mortality and abnormal behavior for each treatment tested. The test will be deemed unacceptable if more than 10% of the test organisms die in the controls.

At 10 days, the wet weights of the surviving *Hyalella azteca* will be determined. Mean organism weight per concentration will be evaluated for comparson with controls.

4.5.3 Test Procedure.- Chemical and Physical. Temperature, dissolved oxygen (DO) and pH will be measured on days 0, 4, 7 and 10 in all test chambers. In addition, temperature and DO will be measured on Days 1 and 2 to determine if the sediment exerts an oxygen demand on the water column. Dissolved oxygen will be maintained at $\geq$40% saturation. (See Section 4.5.5.)

Temperature will be measured continuously in at least one of the test chambers throughout the study. The alkalinity, hardness, and conductivity will

be measured on the dilution water at the beginning of the test and on pooled replicates from each treatment on Day 10.

4.5.4 Preventive Maintenance. Comprehensive maintenance will be performed to provide an organized series of actions (including equipment cleaning, lubricating, reconditioning, adjustments and/or testing) in order to maintain proper instrument and equipment performance, and to prevent instruments and equipment from failing during use. The temperature-controlled water bath, illumination source, thermometer, pH meter, dissolved oxygen meter and conductivity meter will be periodically serviced and maintained in accordance with the manufacturers' instructions. The ABC Laboratories Quality Assurance Unit will monitor the tests to insure that the equipment functions in conformance with good laboratory practice regulations and the protocol for the study.

4.5.5 Trouble Shooting/Corrective Action. If a problem arises in the laboratory, action to correct the problem will be taken promptly. Corrective actions associated with maintaining proper temperature control, illumination and dissolved oxygen levels are discussed below. (See Section 8.0 for sponsor authorization of study changes.)

Temperature - If the temperature-controlled water bath fails to maintain the temperature at 20 ± 2°C, the test will be terminated immediately. The malfunctioning temperature-control system will either be replaced or repaired. The test will be re-started with a fresh inoculation of sediments and amphipods.

Illumination - If the illumination source fails to maintain a light intensity of 70 to 100 foot-candles (and a 16-hour daylight photoperiod), the test will be terminated immediately and the malfunctioning illumination source will either be replaced or repaired. The test will be re-started with a fresh inoculation of sediments and amphipods.

Dissolved Oxygen - If the dissolved oxygen falls below 40% saturation in any test chamber, aeration will be initiated at once and all test chambers. A gentle flow of clean dry air will be supplied through Pasteur pipets connected to the ABC Laboratories in-house air line.

4.6. Analysis of results. Means and standard deviations will be reported where appropriate. The results of the definitive study will be statistically analyzed for differences in survival and growth (live biomass) between impacted, background and control sediments. These analyses will employ appropriate statistical techniques, including analysis of variance techniques complemented with a comparison of treatment means test (17, 18) using PC DOS SAS/STAT Release 6.03.

4.7 Report. One copy of the report will be submitted. The report will contain all original raw data. A copy of the report and associated raw data copies will be held on file in ABC Laboratories' archives. Additional copies will be provided, if requested by the sponsor, at an additional cost. The report will include, but will not be limited to, the following:

4.7.1 Study dates, name and address of test facility.

4.7.2 Objectives and test methods.

4.7.3 Reference to the statistical methods used for data analysis.

4.7.4 Description of test sediment (date of collection, date of receipt, storage conditions, physical characteristics, and method of preparing test chambers).

4.7.5 Description of test design.

4.7.6 Summary of the data analysis, mortality observations, and test water quality.

4.7.7 Location of raw data.

4.7.8 List and signatures of study personnel.

4.7.9 GLP compliance statement by study director and a statement by ABC Laboratories' quality assurance unit.

4.7.10 The report will contain the original raw data for biological observations and water quality, letters of authorized protocol changes and the approved protocol. Any deviations from the study protocol will be noted and their relevance to the test results will be discussed.

5.0 DATA RETENTION

All original raw data generated in the definitive studies will be provided to the study sponsor in the appendix to the final report. A copy of the data will be retained in ABC Laboratories' archives.

6.0 PROTOCOL CHANGES

In the event that modifications of this protocol are deemed necessary, a written statement of any changes and reason(s) proposed by the study

sponsor/study director or ABC Laboratories will be submitted to the other party. All agreed changes will be expressed in writing, signed and dated by the sponsor's representative. The signed changes will be appended to the protocol and included with the final report.

7.0 ANALYTICAL BIO-CHEMISTRY LABORATORIES' QUALITY ASSURANCE UNIT

The ABC quality assurance unit monitors each project to insure that facilities, equipment, personnel, practices, procedures records and controls are designed and function in conformance with good laboratory practice regulat s and the protocol for that study. The quality assurance unit will make frequent, unscheduled inspections of record books, raw data sheets, equipment and all facilities at ABC Laboratories, and will provide written documentation of its observations to laboratory management. Any necessary corrective action will be taken immediately.

8.0 SPONSOR AUTHORIZATIONS DURING THE STUDY

Should a problem develop while the study is in progress, ABC Laboratories will notify the sponsor's representative within 24 hours. The problem and suggested test modifications will be discussed by telephone. ABC Laboratories will proceed with the changes felt necessary upon the verbal authorization of the sponsor's representative. Written acknowledgement will then be submitted by ABC Laboratories to the sponsor's representative and the USEPA.

9.0 TEST-SPECIFIC INFORMATION

9.1.1 General. The following items will be addressed for each bioassay. This information is necessary to be in compliance with Good Laboratory Practice regulations (8). Sections 9.2, 9.3, 9.6.1 and 9.7 are to be completed by the study sponsor. Sections 9.4, 8.5, 9.6.2 and 9.6.3 will be completed by ABC Laboratories.

9.1.2 GLP Compliance. To be in compliance with Federal Good Laboratory Practice regulations, the report of the investigation conducted utilizing this protocol must contain a statement that the study was conducted in accordance with GLP's. The specific GLP regulation, for which this study specific protocol and resultant study must be in compliance with, is the following: U.S. EPA Good Laboratory Practice Standards; Pesticide Programs (40 CFR 160).

9.2 Study Sponsor:

9.2.1 Company _____

9.2.2 Address _____

_____

9.2.3 Sponsor's Representative

_____ _____

Name (Type or Print) Title

9.3 Test Material:

9.3.1 Name _____

9.3.2 Lot/Batch Number _____

9.3.3 Physical Description _____

9.3.4 Date of Collection _____

9.3.5 Handling Precautions. Chemical anaylses of sediment samples collected during February, 1990 indicated that leves of several inorganic constituents in Target Pond are above background levels. The sediment samples will be handled in accordance with Section 8 of ASTM Document E 1391. Briefly, the sediment will be handled to avoid exposure to humans. Laboratory personel will use laboratory coats, aprons, safety glasses and gloves when handling the sediments or test water over the sediments.

9.3.6 Known or suspected source(s) of toxicants (specific industry, waste water treatment, etc.)_____

_____

9.4 Study Dates:

9.4.1 Proposed starting date of definitive study _____

9.4.2 Proposed completion date of definitive study _____

9.5 ABC Laboratories' Study Personnel:

9.5.1 Study Director

_____ _____
Name Title

9.5.2 Aquatic Supervisor

_____ _____
Name Title

9.5.3 Aquatic Manager

_____ _____
Name Title

9.6 Protocol Approvals: The following is to be signed by the appropriate study personnel:

9.6.1 Sponsor's Representative

_____ _____ _____
Signature Title Date

9.6.2 ABC Laboratories' Study Director

_____ _____ _____
Signature Title Date

9.7 Authorization to return or dispose of test sediments

9.7.1 At the conclusion of the study, the remaining sediment and test water will be returned to the study sponsor for disposal. The test material will be returned to the appropriate sampling location in the field.

9.7.2 Sponsor's authorized agent to receive the test material and sample.

_____ _____
Name Title

9.7.3 Shipping Address

Company

Street Address

City State Zip Code

Phone Number

TABLE 1

Chemical Characteristics of Hard Blended Water Used
by ABC Laboratories' Aquatic Toxicology Division[a]

Parameter	Concentration
pH	7.2 - 7.8
Hardness ($CaCO_3$)	160 - 180 mg/L
Alkalinity ($CaCO_3$)	160 - 210 mg/L
Conductivity	220 - 400 μMhos/cm
Suspended Solids	0.2 - 2.2 mg/L
Aluminum	<0.2 mg/L
Arsenic	<1.0 μg/L
Boron	0.582 mg/L
Cadmium	<0.005 mg/L
Chromium	<0.010 mg/L
Cobalt	<0.050 mg/L
Copper	0.033 mg/L
Fluoride	0.98 mg/L
Iron	0.332 mg/L
Lead	12.2 μg/L
Mercury	<0.4 μg/L
Nickel	<0.040 mg/L
Silver	<1.0 μg/L
Zinc	0.067 mg/L

[a] Blended water is a mixture of reverse osmosis (R.O.) and ABC Laboratories' well water to achieve a final hardness of between 160 - 180 mg/L.

Note: The ranges of these selected parameters are from the time period January through October, 1990. All raw data supporting these ranges are on file at ABC Laboratories.

10.0 REFERENCES

(1) U.S. Congress. 1976. Toxic Substances Control Act. Public Law 94-469. Federal Register, October 11, 1976. 2003-2051.

(2) U.S. Congress. 1972. Federal Insecticide, Fungicide, and Rodenticide Act. Public Law 92-516. Federal Register, October 21, 1972.

(3) U.S. Congress. 1977. Clean Water Act of 1977. Public Law 95-217. Federal Register, December 27, 1977: 1566-1611.

(4) U.S. Environmental Protection Agency. 1982. Pesticide Assessment Guidelines, Subdivision E, Hazard Evaluation: Wildlife and Aquatic Organisms. National Technical Information Service, PB83-153908, EPA 540/9-82-024, October 1982.

(5) U.S. Environmental Protection Agency. 1987. Toxic Substances Control Act Test Guidelines; Final Rules. Federal Register, May 20, 1987, 40 CFR parts 796, 797, and 798, Vol. 50 (No. 188).

(6) Adams, W.J., R.A. Kimerle, and R.G. Mosher. 1985. Aquatic Safety Assessment of Chemicals Sorbed to Sediments. Aquatic Toxicology and Hazard Assessment: Seventh Symposium, ASTM STP 854, R.D. Cordwell, R. Purdy, and R.C. Bachner, Eds., American Society for Testing and Materials, Philadelphia, pp. 429-454.

(7) Lynch, T.R. and H.E. Johnson, 1982. Availability of a Hexachlorobiphenyl Isomer to Benthic Amphipods from Experimentally Contaminated Natural Sediments. Aquatic Toxicology and Hazard Assessment. Fifth Conference, ASTM STP 766, J.G. Pearson, R.B. Foster, and W.E. Bishop, Eds., American Society for Testing and Materials, pp. 273-287.

(8) U.S. Environmental Protection Agency. 1989. Federal Insecticide, Fungicide and Rodenticide Act (FIFRA); Good Laboratory Practice Standards; Final Rule (40 CFR, Part 160). Federal Register, Vol. 54; No. 158:34067-34074.

(9) American Society for Testing and Materials. 1980. Standard Practice for Conducting Basic Acute Toxicity Tests with Fish, Macroinvertebrates and Amphibians. May, 1980, ASTM Committee E-35.23. 25 p.

(10) Committee on Methods for Toxicity Tests with Aquatic Organisms 1975. Methods for Acute Toxicity Tests with Fish, Macroinvertebrates and Amphibians. Environmental Protection Agency, Ecological Research Series EPA-660/3-75-009, April, 1975. 61 p.

(11) U.S. Environmental Protection Agency. 1985. Standard Evaluation Procedure, Acute Toxicity Test for Freshwater Invertebrates. 540 9-85-005, June, 1985.

(12) U.S. Food and Drug Administration. 1987. Environmental Assessment Technical Assistance Handbook. *Hyalella azteca* Acute Toxicity. No. 4.10, March, 1987.

(13) Borgmann, U, K.M. Ralph and W.P. Norwood. 1989. Toxicity test procedures for *Hyalella azteca*, and chronic toxicity of cadmium and pentachlorophenol to *Hyalella azteca*, *Gammarus fasciatus* and *Daphnia magna*. Arch. Environm. Contam. Toxicol. 18:(in review).

(14) Nebeker, A.V., S.T. Onjukka, M.A. Cairns and D.F. Krawczyk. 1986. Survival of *Daphnia magna* and *Hyalella azteca* in cadmium spiked water and sediment. Environm. Toxical and Chem. Vol. 5, pp. 933-938.

(15) American Society for Testing and Materials. 1990. Standard Guide for Conducting Sediment Toxicity Tests with Freshwater Invertebrates. Document #1 E 1383. November, 1990, ASTM Subcommittee E47.03. 43 p.

(16) American Society for Testing Materials, 1990. Standard Guide for Collection, Storage, Characterization and Manipulation of Sediments for Toxicology Testing. Document #1 E 1391. November, 1990, ASTM Subcommittee E47.03. 56 p.

(17) Sokal, R.R. and F.J. Rohlf. 1981. Biometry. 2nd ed. W.H. Freeman and Co., San Francisco, California.

(18) Chew, V. 1977. Comparisons Among Treatment Means in an Analysis of Variance. U.S. Department of Agriculture Technical Bulletin No. ARS/H/6. 64 pp.

pH ELECTRODE METHOD
(OPH)

A. Introduction

1. Applicability: This method is applicable to aqueous samples without significant amounts of particulates,oils or greases Method 9040 specifies aqueous phase at ≥20% of total.
2. Purpose of Testing: pH is a parameter which helps to establish corrosivity and/or reactivity of a substance. When the substance is a waste, the information becomes useful in determining proper storage and disposal. It is also helpful for the safe and proper handling of the waste in the course of performing other analyses.
3. Method Detection Limit: N/A. However, method range is 1.0 s.u. to 14.0 s.u. Report all pH measurements by electrode to the nearest 0.5 s.u.
4. Reference Methods: RCRA SW-846, 3rd edition, Rev. 0, Method 9040.
5. Summary of Method: An aliquot of sample is tested with a pH meter using a pH electrode and a reference electrode.
6. Interferences: Soils and oils may inhibit activity at the membrane. The electrode should be kept as free from such materials as possible. When this type of interference is suspected, the paper pH method should be considered an option (See **pH PAPER (PH)**).
7. Sample Collection and Preservation: Samples usually are examined for pH on arrival; otherwise, please reference **Sample Storage** SOP.
8. Holding Time: 24 hours.
9. Safety Precaution: Most waste samples being analyzed for pH are known or suspected hazardous wastes. Extreme caution should be exercised when handling these samples. Lab coats, safety glasses, gloves, and fume hoods are strongly recommended.

B. Apparatus

1. pH meter
2. pH electrode and reference electrode.
3. 100 ml beakers.

C. Reagents and Standards

1. Reagents:
   a. Buffers, traceable to NIST standards, at pH 4,7,10.
2. Standards: Not applicable.
3. Calibration Verification Source: Not available.
4. Spiking Protocol: Not applicable.

D. Method

1. Calibrate the pH meter between two buffer solutions, either 4 and 7 or 7 and 10, depending on the suspected pH of the sample. In order to calibrate, enter the theoretical values of each buffer into the pH meter. Read the low buffer. Allow the reading to equilibrate and set it equal to the theoretical value. Read the high buffer and repeat the same operation. Once this is done, read both buffers. They should be within 0.05 s.u. of their theoretical values. Repeat calibration until this is so.

2. Take a 50 ml aliquot of sample and transfer it to a 100 ml beaker. Immerse the electrode(s) in the sample and allow the reading to equilibrate at the 0.1 level. Disregard smaller fluctuations in precision . Record the pH, noting that the value is entered in the pH-waters log.

E. Calculations

1. pH is read directly from the pH meter.

F. Quality Control

1. Matrix Duplicate: A duplicate analysis for pH should be performed on one of every 20 samples. The relative percent difference should be no more than 30%.

STANDARD
OPERATING
PROCEDURE

Subject or Title: pH (Soils and Wastes)		Page 1 of 6
SOP No.: LM-RMA-1047	Revision No.: 3.1	Effective Date: 9/2/91
Supersedes: Rev. 3.0		

ENSECO PROPRIETARY INFORMATION STATEMENT

1. Scope and Application

   1.1 Analytes

   This method is applicable to the determination of pH.

   1.2 Reporting Limit

   A reporting limit for pH is not defined.

   1.3 Applicable Matrices

   This method is applicable to wastes, oils and soils, both calcareous (high calcium containing) and non-calcareous. If there is uncertainty as to the type of soil being analyzed, the soil will be treated as non-calcareous.

Prepared by:	Date: 9/3/91
Management Approval:	Date: 9/3/91
QA Officer Approval:	Date: 9/3/91

1.4 Dynamic Range

The normal range is from 1 to 10 pH units. Errors at higher pH may be reduced by using a low-sodium-error electrode.

1.5 Analysis Time

Preparation time is about 90 minutes. Approximate analytical time is 5 minutes per sample.

2. Method Summary

The sample is mixed with deionized water; if calcareous (high calcium containing) soil samples are being analyzed, a calcium chloride solution is used instead of water. The pH is then measured electrochemically.

3. Comments

3.1 Interferences

3.1.1 Incorrect results may occur at very high (>10) or very low (<1) pH. Errors at high pH may be reduced by using a low-sodium-error electrode.

3.1.2 Temperature fluctuations will cause measurement errors.

3.1.3 Oil may coat the electrode and interfere with response.

3.2 Helpful Hints

3.2.1 pH values of soils in 0.01M CaCl2 tend to be just slightly lower than but highly correlated with those in water.

4. Safety Issues

4.1 All employees are expected to be familiar with and follow the procedures outlined in the Enseco/RMAL safety plan. Lab coats and safety glasses are required in all laboratory areas at all times. If you have any questions or safety concerns, see your supervisor or safety officer.

4.2 All samples should be considered potentially hazardous and handled with appropriate caution. Wear gloves and handle in a hood as much as possible.

STANDARD
OPERATING
PROCEDURE

SOP No.: LM-RMA-1047	Revision No.: 3.1	Effective Date: 9/2/91

5. Samples Collection, Preservation, Containers, and Holding Times

   5.1 Samples are to be collected in suitable wide-mouth containers and stored at 4°C.

   5.2 There is no holding time for pH on soil samples. Samples, however, must be analyzed within 24 hours of mixing with deionized water.

6. Apparatus

   6.1 pH meter and electrodes. A combination electrode may be used.

   6.2 Beakers and other miscellaneous apparatus and glassware.

   6.3 Glass wool.

7. Reagents and Standards

   7.1 Buffers -- pH 4, 7, and 10. Obtain commercially.

   7.2 Calcium Chloride, 0.01 M

   Dissolve 1.47 g Calcium Chloride Dihydrate in deionized water and dilute to 1000 mL. Check the pH and adjust if necessary to between 5 and 6.5 with calcium hydroxide or hydrochloric acid. The conductance of this solution should be 2320 ± 80 umho/cm at 25°C.

   7.3 DCS (Duplicate Control Sample)

   Obtain a reference material with a certified value for pH. Sources include NTIS and various commercial suppliers. The true value for this material will vary from source to source, but must be established independently of the buffers used for calibration. For example, the minerals control sample from Environmental Resource Associates typically has a "true" pH of 9.2. The material is prepared according to the manufacturer's instructions.

8. Procedure

   8.1 Wastes, Oils, and Non-calcareous Soils

STANDARD OPERATING PROCEDURE

SOP No.: LM-RMA-1047	Revision No.: 3.1	Effective Date: 9/2/91

8.1.1 Weigh 20 g sample into a beaker and add 20 mL deionized water. Mix occasionally over the next 30 minutes.

8.1.2 Let the sample settle undisturbed for 1 hour and then measure the pH as given below. If the samples are oily, filter through glass wool to remove oil, retain the aqueous phase for analysis.

8.2 Calcareous (high calcium containing) Soils

8.2.1 Weigh 10 g sample into a beaker and add 20 mL 0.01 M calcium chloride. Mix occasionally over the next 30 minutes.

8.2.2 Let the sample settle undisturbed for 30 minutes and then measure the pH as given below.

8.3 Measurement of pH

8.3.1 Calibrate the pH meter using at least 2 buffers in the range expected for the samples (pH 4 and 7 for acidic samples, pH 7 and 10 for alkaline samples).

8.3.2 Insert the electrode into the aqueous layer just far enough to cover the electrode bulb and junction. Do not allow the electrode to come into direct contact with oil.

8.3.3 Allow the reading to stabilize and record the pH. Rinse the electrodes well between measurements.

9. QA/QC Requirements

9.1 QC Samples

9.1.1 The prep blank for soil pH is 40 mLs DI water. The blank should be prepped with the samples.

9.1.2 Two DCSs are required with each batch of 20 or less samples.

9.1.3 A standard check and a blank check are required after every 10 or less samples and at the end of the run. Any of the calibration buffers or DCS solution may be used for the standard check.

9.1.4 Duplicates may be required for project specific QC.

9.1.5 It is not possible to spike samples for pH.

9.1.6 See Enseco SOP M-EQA-002 and the Enseco QAPP for additional information.

9.2 Acceptance Criteria

9.2.1 DCS recovery must be 98 to 102%.

9.2.2 The RPD for DCS samples must be less than 5%.

9.2.4 Standard checks must be within 2% of the expected value.

9.2.5 There are no acceptance criteria for project specific QC.

9.2.6 See Enseco SOP M-EQA-002 for additional information.

9.3 Corrective Action Required

9.3.1 Check buffers and DCS to ensure that the expiration dates have not been exceeded. Replace solutions if necessary.

9.3.2 Check the electrodes and clean them if necessary. Replace filling solutions.

9.3.3 Check electrode slope. If less than 98% of theoretical Nernstian value, the electrode should be replaced.

9.3.4 Recalibrate the meter and recheck against DCS.

9.3.5 Reanalyze all affected samples.

9.3.6 Consult supervisor if problems persist.

10. Calculations

There are no calculations for pH.

STANDARD
OPERATING
PROCEDURE

SOP No.: LM-RMA-1047	Revision No.: 3.1	Effective Date: 9/2/91

11. Reporting Requirements

11.1 Results are reported in pH units.

11.2 Significant Figures

Report results to one decimal place (± 0.1 unit).

11.4 LIMS Data Entry

The usual standards for data entry apply.

12. References

12.1 Method source: SW-846 3rd Edition Method 9045, ASTM D 2110-78(B).

12.2 Additional Information: Methods of Soil Analysis, 2nd Edition

12.3 Deviations from source method and rationale
The calcium chloride solution is not initially prepared as a concentrate. It is not standardized against silver nitrate.

12.4 Oily samples are handled by procedures based on ASTM D2110-78(B), pH of Water Extracts of Halogenated Organic Solvents and Their Admixtures. Deionized water is used instead of boiled distilled water, and phase separation is achieved using glass wool rather than separatory funnels.

12.5 Related Documents:

12.4.1 LM-RMA-1071 pH, Alkalinity, Conductance (Autotitrator)

12.4.2 LM-RMA-1091 pH (Manual Method)

12.4.3 M-EQA-002 Internal QC Checks - Laboratory Performance QC

12.4.4 Enseco QAPP

12.5 Updates to SOP

Version 2.0 was updated to Version 3.0 to include provision for analysis of a prep blank.

STANDARD OPERATING PROCEDURE

Subject or Title: TOTAL ORGANIC CARBON IN SOILS & SEDIMENTS

Page 1 of 6

SOP No.:	Revision No.:	Effective Date:
LM-RMA-1116	ORIGINAL	SEPTEMBER 3, 1991

Supersedes: N/A

ENSECO PROPRIETARY INFORMATION STATEMENT

1. Scope and Application

1.1 Analytes

This method covers the determination of total organic carbon using the Dohrmann DC-80 TOC analyzer.

1.2 The detection limit is 100 mg/kg.

1.3 Applicable Matrices

This method is applicable to soils, sludges, and sediments.

Prepared by: Anne Lang	Date: September 3, 1991
Management Approval:	Date: 9/3/91
QA Officer Approval:	Date: 9/3/91

SOP No.:	Revision No.:	Effective Date:
LM-RMA-1116	ORIGINAL	SEPTEMBER 3, 1991

1.4 Dynamic Range

Instrument response is linear to 4000 mg/kg. Higher concentrations may be analyzed by dilution of the samples.

1.5 Approximate analytical time is 5 minutes per sample.

2. Summary of Method

The sample is treated with HCL to drive off inorganic carbonates. Organic carbon in the sample is converted to carbon dioxide (CO_2) by catalytic combustion. The CO_2 formed is measured by an infrared detector. The amount of CO_2 is directly proportional to the concentration of carbonaceous material in the sample.

3. Comments

3.1 Oily samples will cause erratic results. This is minimized by homogenization of the sample.

4. Safety Issues

Follow normal laboratory precautions.

5. Sampling

Samples are collected in glass jars and kept at a temperature of 4°C and protected from sunlight and atmospheric oxygen.

6. Apparatus

6.1 Dohrmann DC-80 TOC Analyzer with sludge/sediment sampler.

6.2 Volumetric pipettes, volumetric flasks, beakers, etc.

7. Reagents and Standards

7.1 10% HCL

Carefully add 10 mLs of concentrated HCL to 90 mLs of deionized water.

7.2 Sodium Persulfate

Add 20 g of $K_2S_2O_8$ to 500 mL of deionized water. Add 1 mL concentrated HNO_3 and dilute to 1000 mL with deionized water.

7.3 TOC calibration Standard, 2000 mg/L

Dissolve 4.256 g potassium hydrogen phthalate in about 600 mL deionized water, add 2 mL concentrated sulfuric acid and dilute to 1000 mLs with deionized water.

7.4 DCS/ICB Solution, 1000 mg/L

Dissolve 2.128 g potassium hydrogen phthalate (use a chemical source independent from that used for the calibration standard) in about 600 mL deionized water, add 2 mL concentrated sulfuric acid, and dilute to 1000 mL with deionized water.

7.5 Silica Gel - baked in muffle furnace prior to use.

8. Procedure

8.1 Sample Prep

8.1.1 A 3-5 g representative aliquot of sample is air dried overnight.

8.1.2 Samples should be homogenized and ground to a very fine mesh. Leave out any extraneous artifacts, ie., glass chards, large twigs and leaves, etc.

8.1.3 On a watch glass add a few drops of 10% HCL to the dried, ground sample. If any fizzing occurs, saturate the sample slowly with 10% HCL. Redry sample. Test for fizzing again. Repeat until no fizzing or no inorganic carbon occurs.

8.1.4 Redry and regrind the sample.

8.2 Instrument Set-up

8.2.1 Turn on furnace and allow about 1/2 hour to warm up.

8.2.2 When furnace is up to temperature (as indicated by an intense red glow) adjust the oxygen to 200 cc/min and turn on the power switch to the detector unit.

STANDARD
OPERATING
PROCEDURE

SOP No.:	Revision No.:	Effective Date:
LM-RMA-1116	ORIGINAL	SEPTEMBER 3, 1991

8.2.3 Prior to running samples make sure that:

- Gas is coming into the UV reactor.
- Water column height difference in the U-tube is approximately 3-4". (This is typical back pressure indicator).
- UV lamp is turned off.
- The reactor is filled with sodium persulfate reagent.

8.2.4 Observe the baseline on the digital display. It should be stable after the furnace temperature is established and all the CO_2 is purged out of the reactor.

8.2.5 The platinum boat may accumulate carbonaceous impurities, mainly from the carrier gas. When the boat has been in the cool zone for a long period of time it should be placed in the furnace for at least two minute to "bake" before use.

8.2.6 Adjust Control Module Settings:

Mode Selection Switch: TOC
Sample Volume Select: 40 uL

8.2.7 Check instrument calibration by analyzing a 2000 mg/L standards. Inject 40 uL of this standard through the septum onto 40 mg of silica gel in the boat. Move the boat into the furnace and press the start button. If result is not within 10%, recalibrate. To erase prior calibration press the CALIB button for more than one second. Then repeat the procedure listed above for three injections of the 2000 mg/L standard. Be sure to let the boat cool for about a minute when removing from the furnace. Press CALIB button to recalibrate. Finally, run a 2000 mg/L standard to check calibration.

9. Analysis

9.1 Remove boat from the flip top inlet block.

9.2 Weigh the combustion boat and record the weight.

9.3 Place about 0.04 g homogenized sediment in the combustion boat and reweigh. Record the weight. Combustion boats should not be handled with the bare hand during this process (use forceps). If total carbon or inorganic carbon is to be determined, cupric oxide fines may be added to the sample to assist in combustion.

9.4 Slide the boat into the furnace.

9.5 Press the start button.

9.6 The result is recorded as total organic carbon.

9.7 Samples which are high in TOC (greater than 4000 mg/kg) are diluted by weight with silica gel. To obtain a homogenous mixture, weighed soil samples are ground with a weighed portion of silica gel to a homogenous powder. An aliquot of around 0.04 g is taken from the diluted sample for analysis.

10. QA/QC Requirements

10.1 QC Samples

10.1.1 Analyze a blank, which is a "baked" boat and 40 mg silica gel, with 40 uL of DI water added with every batch of 20 or less samples.

10.1.2 Two OCS samples are required with every batch of 20 or less samples.

10.1.3 Check standards are required after every 10 or less samples and at the end of the run.

10.1.4 Duplicates may be required as project specific QC.

10.1.5 Spikes may be required as project specific QC. Inject 40 uL of 1000 mg/L stock onto the soil sample in the boat. The spiking concentration is 1000 mg/kg.

10.1.6 If dilutions are needed run a silica gel blank along with the samples.

10.2 Acceptance Criteria

STANDARD
OPERATING
PROCEDURE

SOP No.:	Revision No.:	Effective Date:
LM-RMA-1116	ORIGINAL	SEPTEMBER 3, 1991

10.2.1 DCS

	Accuracy	Precision
TOC	85-115%	20%

10.2.2 Standard checks must be within 10% of the expected value.

10.2.3 Blanks must be less than two times the reporting limit.

10.3 Corrective Action Required

10.3.1 Verify that the instrument is properly calibrated.

10.3.2 Check gas flows with a flow meter at various points through out the system. Repair any leaks.

10.3.3 Check for non-linearity and also the IR output. If results are erratic the cell may need cleaning.

11. Calculations

$$\text{mg/kg C} = \frac{0.04}{\text{Sample Weight}} \times \text{Instrument Reading}$$

Multiply by any dilutions made to get the final result.

12. Reporting

12.1 Reporting units are mg/kg.

12.2 Reporting Limits

Samples less than 100 mg/kg are reported as ND.

12.3 Significant Figures

Three significant figures are reported.

13. References

13.1 EPA Method 415.1

13.2 SW-846 Method 9060

13.3 Dohrmann DC-80 Total Organic Carbon Systems Manual Edition 11.

STANDARD
OPERATING
PROCEDURE

Subject or Title: Page 1 of 9

Total, Fixed and Volatile Solids
Percent Water
(Soils/Wastes)

SOP No.:	Revision No.:	Effective Date:
LM-RMA-1100	2.0	March 14, 1991

Supersedes:
Revision 1.0 (October 30, 1989)

1. Scope and Application

1.1 Analytes

This method determines the Total Solids content of a sample as well as its Fixed and Volatile fractions. These parameters are also referred to as Total, Ash or Non-Volatile, and Volatile Residues, respectively. Percent water is also determined.

Prepared by: Sherman Gray / Will Pratt	Date: March 14, 1991
Management Approval: Will Pratt	Date: 9/3/91
QA Officer Approval: Gary Tofe	Date: 9/3/91

1.2 Reporting Limit

The reporting limit for each parameter is 0.1 percent.

1.3 Applicable Matrices

This method is applicable to soil and industrial/domestic waste samples.

1.4 Dynamic Range

The test range for each parameter is from 0.1 % to 100 %.

1.5 Analysis Time

The approximate analytical time is twenty four hours per sample including preparation and clean up. Multiple analyses can be performed at one time.

2. Method Summary

2.1 A 15 g aliquot of homogenized sample is oven-dried at 105°C. The dried sample is weighed and the Total Solids content is determined.

2.2 The dried sample is ignited at 550°C. The ignited sample is weighed and the Fixed Solids content is determined.

2.3 The Volatile Solids content is determined by difference.

2.4 Percent water is also determined by difference.

3. Comments

The Fixed and Volatile Solids results are expressed as a percentage of the Total Solids content of the sample, NOT as a percentage of the total sample.

The Percent Water result is used to calculate "dry weight" results for other analyses. This calculation is performed automatically by LIMS.

3.1 Interferences

3.1.1 The principal source of error is failure to obtain a representative sample.

3.1.2 Negative errors will result from, among others, evaporative losses, loss of water of crystallization and loss of volatile organic matter during drying.

3.1.3 Positive errors will result from the presence of significant amounts of oil and grease as well as the absorption of moisture after drying or ignition.

3.1.4 Determining low concentrations of Volatile Solids in the presence of high concentrations of Fixed Solids may result in considerable negative error due to occlusion.

3.2 Helpful Hints

Perform all weighings as quickly as possible. Wet samples lose weight through evaporation while dried or ignited samples can be very hygroscopic and absorb moisture from the air.

4. Safety Issues

4.1 All employees are expected to be familiar with and follow the procedures outlined in the Enseco/RMAL safety plan. A lab coat and safety glasses are required in all laboratory areas at all times. If you have any questions or safety concerns, see your supervisor or safety officer.

4.2 High temperature ovens are employed in this procedure. Adequate gloves and tongs should be used when transferring samples from the ovens samples.

5. Sample Collection, Preservation and Holding Times

5.1 Samples are to be collected in a glass or plastic bottle with a tight fitting cap and refrigerated to 4°C.

5.2 There is no holding time for these parameters, however, analysis should begin as soon as possible.

6. Apparatus

6.1 Aluminum weigh dishes.

6.2 Top-loading balance, 0.01 g sensitivity.

6.3 Drying oven (110°C capacity).

6.4 Muffle furnace (600°C capacity).

6.5 High temperature gloves.

6.6 Crucible tongs, long handled.

6.7 Desiccator.

7. Reagents and Standards

7.1 Desiccant (anhydrous sodium sulfate or equivalent).

8. Procedure

8.1 Instrument Set-up and Calibration

8.1.1 Turn on the drying oven and set the temperature for 105°C.

8.1.2 Turn on the muffle furnace and set the temperature for 550°C.

8.2 Preparation

8.2.1 Identify the samples and tests to be analyzed using the backlogs.

8.2.2 For samples requiring Total Solids (or Percent Water) only, place new, numbered aluminum weigh dishes in a preheated drying oven for 1 hour at 105°C. For samples requiring Fixed or Volatile Solids, place new, numbered aluminum weigh dishes in a preheated muffle furnace for 1 hour at 550°C. Remove, cool and store all weigh dishes in a desiccator until ready for use.

8.2.3 Check LIMS for Special Instructions for EVERY sample. Make copies whether they apply or not, include them with the data package and record on the benchsheet.

8.2.4 Obtain the samples to be analyzed from the walk-in cooler. Record the sample numbers on the benchsheet.

8.3 Analysis

For all analytes, sample masses are determined by first taring the balance with an empty weigh dish. BE CAREFUL NOT TO TARE THE BALANCE AGAIN PRIOR TO OBTAINING THE SAMPLE MASS. It has been found that the aluminum weigh dishes do not vary in mass more than 0.02 gram.

8.3.1 Remove a pretreated aluminum weigh dish from the desiccator, place on the top-loading balance and tare the balance. Record the weigh dish number on the benchsheet.

8.3.2 Homogenize the sample and pulverize large chunks. Place a 15.0 gram aliquot into the dish. Record the wet sample mass to the nearest 0.01 gram on the benchsheet.

8.3.3 Carefully place the sample and dish in the preheated drying oven. Allow the sample to dry for between 12 and 24 hours.

NOTE: Samples may be dried for less than 12 hours as long as the weight loss between drying cycles is no more than 0.01 g. Consult your supervisor before proceeding, however.

8.3.4 Remove and immediately place the dried samples in a desiccator. Allow to cool for one hour. If the sample appears oily, record on the benchsheet.

8.3.5 Tare the balance with an empty weigh dish. Weigh the dried sample and record the mass on the benchsheet. Total Solids (and Percent Water) may now be calculated. See section 10.1.

NOTE: If NEITHER Fixed NOR Volatile Solids determinations are required, proceed to section 8.4.

8.3.6 Carefully place the dried sample and dish in the preheated muffle furnace. Allow the sample to ignite for 1 hour at 550°C.

8.3.7 Remove and immediately place the ignited samples in a desiccator. Allow to cool for one hour.

8.3.8 Again tare the balance with an empty weigh dish. Weigh the ignited sample and record the mass on the benchsheet. Fixed and Volatile Solids may now be calculated. See sections 10.2 and 10.3, respectively.

8.4 Conclusion

8.4.1 Dispose of the "spent" sample in a properly labelled waste container.

8.4.2 Return all unused samples to the walk-in cooler.

8.4.3 Turn off all equipment, clean all apparatus and work area.

8.4.4 Complete the data package making sure the benchsheet is properly filled out (see attached example-Attachment I). Submit to supervisor for approval.

9. QA/QC Requirements

9.1 QC Samples

9.1.1 A blank is not applicable to Solids analyses.

9.1.2 DCSs are not applicable to Solids analyses.

9.1.3 Duplicates may be required for project specific QC.

9.1.4 Spikes are not applicable to Solids analyses.

9.1.5 See SOP: M-EQA-0002 and the Enseco QAPP.

9.2 Acceptance Criteria

There are no acceptance criteria for Solids analyses.

9.3 Corrective Actions

Follow the corrective actions outlined in the current Enseco QA Plan.

10. Calculations

10.1 Total Solids, % = $\left\{\frac{B}{A}\right\} * 100$

10.2 Fixed Solids, % = $\left\{\frac{C}{B}\right\} * 100$

10.3 Volatile Solids, % = $\left\{\frac{B - C}{B}\right\} * 100$

10.3 Percent Water, % = $100 - \left[\left\{\frac{B}{A}\right\} * 100\right]$

where "A" is the sample mass, wet (grams),
"B" is the sample mass, dry (grams) and
"C" is the sample mass, ignited (grams).

Volatile Solids may also be calculated as
100 - % Fixed Solids (see attached benchsheet example).

11. Reporting Requirements

11.1 Units

The reporting unit for Total Solids and Percent Water is % (of total sample).

The reporting unit for Fixed and Volatile Solids is % (of total solids).

STANDARD
OPERATING
PROCEDURE

SOP No.:	Revision No.:	Effective Date:
LM-RMA-1100	2.0	March 14, 1991

11.2 Limits

The reporting limit for all parameters is 0.1 %.

11.3 Significant Figures

All results are to be reported to the nearest 0.1 %.

11.4 LIMS Data Entry

ALL Fixed Solids and Volatile Solids results are footnoted "Reported as a percentage of total solids content" (LIMS footnote "v").

11.5 Anomalies

Results from samples that appear oily after the drying cycle are anomalized "Results of sample XX may be inaccurate - sample appeared oily after drying".

12. Review Requirements

12.1 Verify that calculations were performed correctly by checking all of them.

12.2 Verify that Fixed Solids and Volatile Solids results are correctly footnoted.

12.3 Verify that results are correctly anomalized.

12.4 Transfer anomalies to preview report cover sheet.

13. References

13.1 Source Methods: Method 160.3 "Total Residue" and Method 160.4 "Volatile Residue", Methods for Chemical Analysis of Water and Wastes, EPA-600, March, 1983; ASTM D2216-80 "Laboratory Determination of Water (Moisture) Content of Soil, Rock and Soil-Aggregate Mixtures."

13.2 Related Documents

13.2.1 Method 2540 G. "Total, Fixed, and Volatile Solids in Solid and Semisolid Samples", Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.

13.2.2 Method 7-2.2. "Gravimetry with Oven Drying", Methods of Soil Analysis, Number 9, C.A. Black, American Society of Agronomy, 1965.

13.3 Deviations from Source Method and Rationale

The EPA source methods specify waters and wastes as the applicable matrices. Deviations in this SOP exist as a result of the different matrices analyzed.

13.3.1 Aluminum weigh dishes are used instead of porcelain as a matter of convenience.

13.3.2 Method 2540 G recommends the use of a 25 - 50 g sample aliquot. 15 g is used since that is the approximate capacity of the aluminum weigh dishes employed.

13.3.3 The 12 to 24 hour drying time window was adapted from the EPA-CLP SOW 787, Part F.

13.3.4 Percent Water is expressed as a simple percentage, not as the ratio of "pore" or "free" water to the mass of solid material, as defined in the ASTM D2216 method.

13.4 Updates to SOP (Original to Revision 1.0)

13.4.1 Nomenclature has been revised (e.g. Fixed vs. Non-Volatile).

13.4.2 The actual weighing of empty dishes has been eliminated to save time during the calculations.

13.4.3 The reference methods were revised and expanded.

13.4.4 Revision 1.0 to Revision 2.0 incorporated the Percent Water analysis and all appropriate calculations and deviations. The example benchsheet has also been revised to reflect Percent Water.

(425-μm) sieve is required in total amount of 220 g, allocated as follows:

Test	Grams
Liquid limit	100
Plastic limit	15
Centrifuge moisture equivalent	10
Volumetric shrinkage	30
Check tests	65

6. Preparation of Test Sample

6.1 Select that portion of the air-dried sample selected for purpose of tests and record the mass as the mass of the total test sample uncorrected for hygroscopic moisture. Separate the test sample by sieving with a No. 10 (2.00-mm) sieve. Grind that fraction retained on the No. 10 sieve in a mortar with a rubber-covered pestle until the aggregations of soil particles are broken up into the separate grains. Then separate the ground soil into two fractions by sieving with a No. 10 sieve.

6.2 Wash that fraction retained after the second sieving free of all fine material, dry, and weigh. Record this mass as the mass of coarse material. Sieve the coarse material, after being washed and dried, on the No. 4 (4.75-mm) sieve and record the mass retained on the No. 4 sieve.

7. Test Sample for Particle-Size Analysis

7.1 Thoroughly mix together the fractions passing the No. 10 (2.00-mm) sieve in both sieving operations, and by the method of quartering or the use of a sampler, select a portion weighing approximately 115 g for sandy soils and approximately 65 g for silt and clay soil for particle-size analysis.

8. Test Sample for Soil Constants

8.1 Separate the remaining portion of the material passing the No. 10 (2.00-mm) sieve into two parts by means of a No. 40 (425-μm) sieve. Discard the fraction retained on the No. 40 sieve. Use the fraction passing the No. 40 sieve for the determination of the soil constants.

Standard Method for PARTICLE-SIZE ANALYSIS OF SOILS[1]

This standard is issued under the fixed designation D 422; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

[4] NOTE—Section 2 was added editorially and subsequent sections renumbered in July 1984.

1. Scope

1.1 This method covers the quantitative determination of the distribution of particle sizes in soils. The distribution of particle sizes larger than 75 μm (retained on the No. 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75 μm is determined by a sedimentation process, using a hydrometer to secure the necessary data (Notes 1 and 2).

NOTE 1—Separation may be made on the No. 4 (4.75-mm), No. 40 (425-μm), or No. 200 (75-μm) sieve instead of the No. 10. For whatever sieve used, the size shall be indicated in the report.

NOTE 2—Two types of dispersion devices are provided: (*1*) a high-speed mechanical stirrer, and (*2*) air dispersion. Extensive investigations indicate that air-dispersion devices produce a more positive dispersion of plastic soils below the 20-μm size and appreciably less degradation on all sizes when used with sandy soils. Because of the definite advantages favoring air dispersion, its use is recommended. The results from the two types of devices differ in magnitude, depending upon soil type, leading to marked differences in particle size distribution, especially for sizes finer than 20 μm.

2. Applicable Documents

2.1 *ASTM Standards:*

D421 Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[3]

E 100 Specification for ASTM Hydrometers[4]

3. Apparatus

3.1 *Balances*—A balance sensitive to 0.01 g for weighing the material passing a No. 10 (2.00-mm) sieve, and a balance sensitive to 0.1 % of the mass of the sample to be weighed for weighing the material retained on a No. 10 sieve.

3.2 *Stirring Apparatus*—Either apparatus A or B may be used.

3.2.1 Apparatus A shall consist of a mechanically operated stirring device in which a suitably mounted electric motor turns a vertical shaft at a speed of not less than 10 000 rpm without load. The shaft shall be equipped with a replaceable stirring paddle made of metal, plastic, or hard rubber, as shown in Fig. 1. The shaft shall be of such length that the stirring paddle will operate not less than ¾ in. (19.0 mm) nor more than 1½ in. (38.1 mm) above the bottom of the dispersion cup. A special dispersion cup conforming to either of the designs shown in Fig. 2 shall be provided to hold the sample while it is being dispersed.

3.2.2 Apparatus B shall consist of an air-jet dispersion cup[5] (Note 3) conforming to the general details shown in Fig. 3 (Notes 4 and 5).

NOTE 3—The amount of air required by an air-jet dispersion cup is of the order of 2 ft³/min; some small air compressors are not capable of supplying sufficient air to operate a cup.

NOTE 4—Another air-type dispersion device, known as a dispersion tube, developed by Chu and Davidson at Iowa State College, has been shown to give

[1] This method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

Current edition approved Nov. 21, 1963. Originally published 1935. Replaces D 422 – 62.

[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] *Annual Book of ASTM Standards*, Vol 14.01.

[5] Detailed working drawings for this cup are available at a nominal cost from the American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103. Order Adjunct No. 12-404220-00.

equiv o thos ed by r-jet d sion cups. When it is used, soaking of the sample can be done in the sedimentation cylinder, thus eliminating the need for transferring the slurry. When the air-dispersion tube is used, it shall be so indicated in the report.

NOTE 5—Water may condense in air lines when not in use. This water must be removed, either by using a water trap on the air line, or by blowing the water out of the line before using any of the air for dispersion purposes.

3.3 *Hydrometer*—An ASTM hydrometer, graduated to read in either specific gravity of the suspension or grams per litre of suspension, and conforming to the requirements for hydrometers 151H or 152H in Specifications E 100. Dimensions of both hydrometers are the same, the scale being the only item of difference.

3.4 *Sedimentation Cylinder*—A glass cylinder essentially 18 in. (457 mm) in height and 2½ in. (63.5 mm) in diameter, and marked for a volume of 1000 mL. The inside diameter shall be such that the 1000-mL mark is 36 ± 2 cm from the bottom on the inside.

3.5 *Thermometer*—A thermometer accurate to 1°F (0.5°C).

3.6 *Sieves*—A series of sieves, of square-mesh woven-wire cloth, conforming to the requirements of Specification E 11. A full set of sieves includes the following (Note 6):

3-in. (75-mm)	No. 10 (2.00-mm)
2-in. (50-mm)	No. 20 (850-μm)
1½-in. (37.5-mm)	No. 40 (425-μm)
1-in. (25.0-mm)	No. 60 (250-μm)
¾-in. (19.0-mm)	No. 140 (106-μm)
⅜-in. (9.5-mm)	No. 200 (75-μm)
No. 4 (4.75-mm)	

NOTE 6—A set of sieves giving uniform spacing of points for the graph, as required in Section 17, may be used if desired. This set consists of the following sieves:

3-in. (75-mm)	No. 16 (1.18-mm)
1½-in. (37.5-mm)	No. 30 (600-μm)
¾-in. (19.0-mm)	No. 50 (300-μm)
⅜-in. (9.5-mm)	No. 100 (150-μm)
No. 4 (4.75-mm)	No. 200 (75-μm)
No. 8 (2.36-mm)	

3.7 *Water Bath or Constant-Temperature Room*—A water bath or constant-temperature room for maintaining the soil suspension at a constant temperature during the hydrometer analysis. A satisfactory water tank is an insulated tank that maintains the temperature of the suspension at a convenient constant temperature at or near 68°F (20°C). Such a device is illustrated in Fig. 4. In cases where the work is performed in a room at an automatically controlled constant te ture, er l not ary.

3.8 *Beaker*—A ker of 250-mL capacity.

3.9 *Timing Device*—A watch or clock with a second hand.

4. Dispersing Agent

4.1 A solution of sodium hexametaphosphate (sometimes called sodium metaphosphate) shall be used in distilled or demineralized water, at the rate of 40 g of sodium hexametaphosphate/litre of solution (Note 7).

NOTE 7—Solutions of this salt, if acidic, slowly revert or hydrolyze back to the orthophosphate form with a resultant decrease in dispersive action. Solutions should be prepared frequently (at least once a month) or adjusted to pH of 8 or 9 by means of sodium carbonate. Bottles containing solutions should have the date of preparation marked on them.

4.2 All water used shall be either distilled or demineralized water. The water for a hydrometer test shall be brought to the temperature that is expected to prevail during the hydrometer test. For example, if the sedimentation cylinder is to be placed in the water bath, the distilled or demineralized water to be used shall be brought to the temperature of the controlled water bath; or, if the sedimentation cylinder is used in a room with controlled temperature, the water for the test shall be at the temperature of the room. The basic temperature for the hydrometer test is 68°F (20°C). Small variations of temperature do not introduce differences that are of practical significance and do not prevent the use of corrections derived as prescribed.

5. Test Sample

5.1 Prepare the test sample for mechanical analysis as outlined in Practice D 421. During the preparation procedure the sample is divided into two portions. One portion contains only particles retained on the No. 10 (2.00-mm) sieve while the other portion contains only particles passing the No. 10 sieve. The mass of air-dried soil selected for purpose of tests, as prescribed in Practice D 421, shall be sufficient to yield quantities for mechanical analysis as follows:

5.1.1 The size of the portion retained on the No. 10 sieve shall depend on the maximum size of particle, according to the following schedule:

Nominal Diameter of Largest Particles, in. (mm)	Approximate Minimum Mass of Portion, g
⅜ (9.5)	500
¾ (19.0)	1000
1 (25.4)	2000
1½ (38.1)	3000
2 (50.8)	4000
3 (76.2)	5000

5.1.2 The size of the portion passing the No. 10 sieve shall be approximately 115 g for sandy soils and approximately 65 g for silt and clay soils.

5.2 Provision is made in Section 5 of Practice D 421 for weighing of the air-dry soil selected for purpose of tests, the separation of the soil on the No. 10 sieve by dry-sieving and washing, and the weighing of the washed and dried fraction retained on the No. 10 sieve. From these two masses the percentages retained and passing the No. 10 sieve can be calculated in accordance with 12.1.

NOTE 8—A check on the mass values and the thoroughness of pulverization of the clods may be secured by weighing the portion passing the No. 10 sieve and adding this value to the mass of the washed and oven-dried portion retained on the No. 10 sieve.

SIEVE ANALYSIS OF PORTION RETAINED ON NO. 10 (2.00-mm) SIEVE

6. Procedure

6.1 Separate the portion retained on the No. 10 (2.00-mm) sieve into a series of fractions using the 3-in. (75-mm), 2-in. (50-mm), 1½-in. (37.5-mm), 1-in. (25.0-mm), ¾-in. (19.0-mm), ⅜-in. (9.5-mm), No. 4 (4.75-mm), and No. 10 sieves, or as many as may be needed depending on the sample, or upon the specifications for the material under test.

6.2 Conduct the sieving operation by means of a lateral and vertical motion of the sieve, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments in the sample through the sieve by hand. Continue sieving until not more than 1 mass % of the residue on a sieve passes that sieve during 1 min of sieving. When mechanical sieving is used, test the thoroughness of sieving by using the hand method of sieving as described above.

6.3 Determine the mass of each fraction on a balance conforming to the requirements of 3.1. At the end of weighing, the sum of the masses retained on all the sieves used should equal closely the original mass of the quantity sieved.

7. Determination of Composite Correction for Hydrometer Reading

7.1 Equations for percentages of soil remaining in suspension, as given in 14.3, are based on the use of distilled or demineralized water. A dispersing agent is used in the water, however, and the specific gravity of the resulting liquid is appreciably greater than that of distilled or demineralized water.

7.1.1 Both soil hydrometers are calibrated at 68°F (20°C), and variations in temperature from this standard temperature produce inaccuracies in the actual hydrometer readings. The amount of the inaccuracy increases as the variation from the standard temperature increases.

7.1.2 Hydrometers are graduated by the manufacturer to be read at the bottom of the meniscus formed by the liquid on the stem. Since it is not possible to secure readings of soil suspensions at the bottom of the meniscus, readings must be taken at the top and a correction applied.

7.1.3 The net amount of the corrections for the three items enumerated is designated as the composite correction, and may be determined experimentally.

7.2 For convenience, a graph or table of composite corrections for a series of 1° temperature differences for the range of expected test temperatures may be prepared and used as needed. Measurement of the composite corrections may be made at two temperatures spanning the range of expected test temperatures, and corrections for the intermediate temperatures calculated assuming a straight-line relationship between the two observed values.

7.3 Prepare 1000 mL of liquid composed of distilled or demineralized water and dispersing agent in the same proportion as will prevail in the sedimentation (hydrometer) test. Place the liquid in a sedimentation cylinder and the cylinder in the constant-temperature water bath, set for one of the two temperatures to be used. When the temperature of the liquid becomes constant, insert the hydrometer, and, after a short interval to permit the hydrometer to come to the temperature of the liquid, read the hydrometer at the top of the meniscus formed on the stem. For hydrometer 151H the composite correction is the difference between this reading and one; for hy-

ieter it is ffere :twee reading and zero. Bring the liquid and the hydrometer to the other temperature to be used, and secure the composite correction as before.

8. Hygroscopic Moisture

8.1 When the sample is weighed for the hydrometer test, weigh out an auxiliary portion of from 10 to 15 g in a small metal or glass container, dry the sample to a constant mass in an oven at 230 ± 9°F (110 ± 5°C), and weigh again. Record the masses.

9. Dispersion of Soil Sample

9.1 When the soil is mostly of the clay and silt sizes, weigh out a sample of air-dry soil of approximately 50 g. When the soil is mostly sand the sample should be approximately 100 g.

9.2 Place the sample in the 250-mL beaker and cover with 125 mL of sodium hexametaphosphate solution (40 g/L). Stir until the soil is thoroughly wetted. Allow to soak for at least 16 h.

9.3 At the end of the soaking period, disperse the sample further, using either stirring apparatus A or B. If stirring apparatus A is used, transfer the soil - water slurry from the beaker into the special dispersion cup shown in Fig. 2, washing any residue from the beaker into the cup with distilled or demineralized water (Note 9). Add distilled or demineralized water, if necessary, so that the cup is more than half full. Stir for a period of 1 min.

NOTE 9—A large size syringe is a convenient device for handling the water in the washing operation. Other devices include the wash-water bottle and a hose with nozzle connected to a pressurized distilled water tank.

9.4 If stirring apparatus B (Fig. 3) is used, remove the cover cap and connect the cup to a compressed air supply by means of a rubber hose. A air gage must be on the line between the cup and the control valve. Open the control valve so that the gage indicates 1 psi (7 kPa) pressure (Note 10). Transfer the soil - water slurry from the beaker to the air-jet dispersion cup by washing with distilled or demineralized water. Add distilled or demineralized water, if necessary, so that the total volume in the cup is 250 mL, but no more.

NOTE 10—The initial air pressure of 1 psi is required to prevent the soil - water mixture from entering the air-jet chamber when the mixture is transferred to the dispersion cup.

lace ver c the ad ope the air control valve until the gage pressure is 2 psi (140 kPa). Disperse the soil according to the following schedule:

Plasticity Index	Dispersion Period, min
Under 5	5
6 to 20	10
Over 20	15

Soils containing large percentages of mica need be dispersed for only 1 min. After the dispersion period, reduce the gage pressure to 1 psi preparatory to transfer of soil - water slurry to the sedimentation cylinder.

10. Hydrometer Test

10.1 Immediately after dispersion, transfer the soil - water slurry to the glass sedimentation cylinder, and add distilled or demineralized water until the total volume is 1000 mL.

10.2 Using the palm of the hand over the open end of the cylinder (or a rubber stopper in the open end), turn the cylinder upside down and back for a period of 1 min to complete the agitation of the slurry (Note 11). At the end of 1 min set the cylinder in a convenient location and take hydrometer readings at the following intervals of time (measured from the beginning of sedimentation), or as many as may be needed, depending on the sample or the specification for the material under test: 2, 5, 15, 30, 60, 250, and 1440 min. If the controlled water bath is used the sedimentation cylinder should be placed in the bath between the 2- and 5-min readings.

NOTE 11—The number of turns during this minute should be approximately 60, counting the turn upside down and back as two turns. Any soil remaining in the bottom of the cylinder during the first few turns should be loosened by vigorous shaking of the cylinder while it is in the inverted position.

10.3 When it is desired to take a hydrometer reading, carefully insert the hydrometer about 20 to 25 s before the reading is due to approximately the depth it will have when the reading is taken. As soon as the reading is taken, carefully remove the hydrometer and place it with a spinning motion in a graduate of clean distilled or demineralized water.

NOTE 12—It is important to remove the hydrometer immediately after each reading. Readings shall be taken at the top of the meniscus formed by the suspension around the stem, since it is not possible to secure readings at the bottom of the meniscus.

10.4 After each reading, take the temperature of the suspension by inserting the thermometer into the suspension.

11. Sieve Analysis

11.1 After taking the final hydrometer reading, transfer the suspension to a No. 200 (75-μm) sieve and wash with tap water until the wash water is clear. Transfer the material on the No. 200 sieve to a suitable container, dry in an oven at 230 ± 9°F (110 ± 5°C) and make a sieve analysis of the portion retained, using as many sieves as desired, or required for the material, or upon the specification of the material under test.

CALCULATIONS AND REPORT

12. Sieve Analysis Values for the Portion Coarser than the No. 10 (2.00-mm) Sieve

12.1 Calculate the percentage passing the No. 10 sieve by dividing the mass passing the No. 10 sieve by the mass of soil originally split on the No. 10 sieve, and multiplying the result by 100. To obtain the mass passing the No. 10 sieve, subtract the mass retained on the No. 10 sieve from the original mass.

12.2 To secure the total mass of soil passing the No. 4 (4.75-mm) sieve, add to the mass of the material passing the No. 10 sieve the mass of the fraction passing the No. 4 sieve and retained on the No. 10 sieve. To secure the total mass of soil passing the ⅜-in. (9.5-mm) sieve, add to the total mass of soil passing the No. 4 sieve, the mass of the fraction passing the ⅜-in. sieve and retained on the No. 4 sieve. For the remaining sieves, continue the calculations in the same manner.

12.3 To determine the total percentage passing for each sieve, divide the total mass passing (see 12.2) by the total mass of sample and multiply the result by 100.

13. Hygroscopic Moisture Correction Factor

13.1 The hydroscopic moisture correction factor is the ratio between the mass of the oven-dried sample and the air-dry mass before drying. It is a number less than one, except when there is no hygroscopic moisture.

14. Percentages of Soil in Suspension

14.1 Calculate the oven-dry mass of soil used in the hydrometer analysis by multiplying the air-dry mass by the hygroscopic moisture correction factor.

14.2 Calculate the mass of a total sample represented by the mass of soil used in the hydrometer test, by dividing the oven-dry mass used by the percentage passing the No. 10 (2.00-mm) sieve, and multiplying the result by 100. This value is the weight W in the equation for percentage remaining in suspension.

14.3 The percentage of soil remaining in suspension at the level at which the hydrometer is measuring the density of the suspension may be calculated as follows (Note 13): For hydrometer 151H:

$$P = [(100\,000/W) \times G/(G - G_1)](R - G_1)$$

NOTE 13—The bracketed portion of the equation for hydrometer 151H is constant for a series of readings and may be calculated first and then multiplied by the portion in the parentheses.

For hydrometer 152H:

$$P = (Ra/W) \times 100$$

where:

a = correction faction to be applied to the reading of hydrometer 152H. (Values shown on the scale are computed using a specific gravity of 2.65. Correction factors are given in Table 1),

P = percentage of soil remaining in suspension at the level at which the hydrometer measures the density of the suspension,

R = hydrometer reading with composite correction applied (Section 7),

W = oven-dry mass of soil in a total test sample represented by mass of soil dispersed (see 14.2), g,

G = specific gravity of the soil particles, and

G_1 = specific gravity of the liquid in which soil particles are suspended. Use numerical value of one in both instances in the equation. In the first instance any possible variation produces no significant effect, and in the second instance, the composite correction for R is based on a value of one for G_1.

15. Diameter of Soil Particles

15.1 The diameter of a particle corresponding to the percentage indicated by a given hydrometer reading shall be calculated according to Stokes' law (Note 14), on the basis that a particle of this diameter was at the surface of the suspension at the beginning of sedimentation and had settled to the level at which the hydrometer is measuring the density of the suspension. Accord-

g to S law:

$$D = \sqrt{[30n/980(G - G_1)]} \times L/T$$

where:

D = diameter of particle, mm,

n = coefficient of viscosity of the suspending medium (in this case water) in poises (varies with changes in temperature of the suspending medium),

L = distance from the surface of the suspension to the level at which the density of the suspension is being measured, cm. (For a given hydrometer and sedimentation cylinder, values vary according to the hydrometer readings. This distance is known as effective depth (Table 2)),

T = interval of time from beginning of sedimentation to the taking of the reading, min,

G = specific gravity of soil particles, and

G_1 = specific gravity (relative density) of suspending medium (value may be used as 1.000 for all practical purposes).

NOTE 14—Since Stokes' law considers the terminal velocity of a single sphere falling in an infinity of liquid, the sizes calculated represent the diameter of spheres that would fall at the same rate as the soil particles.

15.2 For convenience in calculations the above equation may be written as follows:

$$D = K\sqrt{L/T}$$

where:

K = constant depending on the temperature of the suspension and the specific gravity of the soil particles. Values of K for a range of temperatures and specific gravities are given in Table 3. The value of K does not change for a series of readings constituting a test, while values of L and T do vary.

15.3 Values of D may be computed with sufficient accuracy, using an ordinary 10-in. slide rule.

NOTE 15—The value of L is divided by T using the A- and B-scales, the square root being indicated on the D-scale. Without ascertaining the value of the square root it may be multiplied by K, using either the C- or CI-scale.

16. Sieve Analysis Values for Portion Finer than No. 10 (2.00-mm) Sieve

16.1 Calculation of percentages passing the various sieves used in sieving the portion of the sample from the hydrometer test involves several steps. The first step is to calculate the mass of the

on th d been ed o No. 10 sieve ha not been removed. This mass is equal to the total percentage retained on the No. 10 sieve (100 minus total percentage passing) times the mass of the total sample represented by the mass of soil used (as calculated in 14.2), and the result divided by 100.

16.2 Calculate next the total mass passing the No. 200 sieve. Add together the fractional masses retained on all the sieves, including the No. 10 sieve, and subtract this sum from the mass of the total sample (as calculated in 14.2).

16.3 Calculate next the total masses passing each of the other sieves, in a manner similar to that given in 12.2.

16.4 Calculate last the total percentages passing by dividing the total mass passing (as calculated in 16.3) by the total mass of sample (as calculated in 14.2), and multiply the result by 100.

17. Graph

17.1 When the hydrometer analysis is performed, a graph of the test results shall be made, plotting the diameters of the particles on a logarithmic scale as the abscissa and the percentages smaller than the corresponding diameters to an arithmetic scale as the ordinate. When the hydrometer analysis is not made on a portion of the soil, the preparation of the graph is optional, since values may be secured directly from tabulated data.

18. Report

18.1 The report shall include the following:

18.1.1 Maximum size of particles,

18.1.2 Percentage passing (or retained on) each sieve, which may be tabulated or presented by plotting on a graph (Note 16),

18.1.3 Description of sand and gravel particles:

18.1.3.1 Shape—rounded or angular,

18.1.3.2 Hardness—hard and durable, soft, or weathered and friable,

18.1.4 Specific gravity, if unusually high or low,

18.1.5 Any difficulty in dispersing the fraction passing the No. 10 (2.00-mm) sieve, indicating any change in type and amount of dispersing agent, and

18.1.6 The dispersion device used and the length of the dispersion period.

NOTE 16—This tabul a of graph represents the gradation of the sample tested. If particles larger than those contained in the sample were removed before testing, the report shall so state giving the amount and maximum size.

18.2 For materials tested for compliance with definite specifications, the fractions called for in such specifications shall be reported. The fractions smaller than the No. 10 sieve shall be read from the graph.

18.3 For materials for which compliance with definite specifications is not indicated and when the soil is composed almost entirely of particles passing the No. 4 (4.75-mm) sieve, the results read from the graph may be reported as follows:

(1) Gravel, passing 3-in. and retained on No. 4 sieve ..... %

(2) Sand, passing No. 4 sieve and retained on No. 200 sieve ..... %

(a) Coarse sand, passing No. 4 sieve and retained on No. 10 sieve ..... %

(b) Medium sand, passing No. 10 sieve and retained on No. 40 sieve ..... %

(c) Fine sand, passing No. 40 sieve and retained on No. 200 sieve ..... %

(3) Silt size, 0.074 to 0.005 mm ..... %

(4) Clay size, smaller than 0.005 mm %

Colloids, smaller than 0.001 mm %

18.4 For materials for which compliance with definite specifications is not indicated and when the soil contains material retained on the No. 4 sieve sufficient to require a sieve analysis on that portion, the results may be reported as follows (Note 17):

Sieve Analysis	
Sieve Size	Percentage Passing
3-in.	
2-in.	
1½-in.	
1-in.	
¾-in.	
⅜-in.	
No. 4 (4.75-mm)	
No. 10 (2.00-mm)	
No. 40 (425-μm)	
No. 200 (75-μm)	
Hydrometer Analysis	
0.074 mm	
0.005 mm	
0.001 mm	

NOTE 17—No. 8 (2.36-mm) and No. 50 (300-μm) sieves may be substituted for No. 10 and No. 40 sieves.

TABLE [illegible] Values of Correction Factor, a, for [illegible] Specific Gravities of Soil Particles[A]

Specific Gravity	Correction Factor[A]
2.95	0.94
2.90	0.95
2.85	0.96
2.80	0.97
2.75	0.98
2.70	0.99
2.65	1.00
2.60	1.01
2.55	1.02
2.50	1.03
2.45	1.05

[A] For use in equation for percentage of soil remaining in suspension when using Hydrometer 152H.

TABLE 2 Values of Effective Depth Based on Hydrometer and Sedimentation Cylinder of Specified Sizes[A]

Hydrometer 151H		Hydrometer 152H			
Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm
1.000	16.3	0	16.3	31	11.2
1.001	16.0	1	16.1	32	11.1
1.002	15.8	2	16.0	33	10.9
1.003	15.5	3	15.8	34	10.7
1.004	15.2	4	15.6	35	10.6
1.005	15.0	5	15.5		
1.006	14.7	6	15.3	36	10.4
1.007	14.4	7	15.2	37	10.2
1.008	14.2	8	15.0	38	10.1
1.009	13.9	9	14.8	39	9.9
1.010	13.7	10	14.7	40	9.7
1.011	13.4	11	14.5	41	9.6
1.012	13.1	12	14.3	42	9.4
1.013	12.9	13	14.2	43	9.2
1.014	12.6	14	14.0	44	9.1
1.015	12.3	15	13.8	45	8.9
1.016	12.1	16	13.7	46	8.8
1.017	11.8	17	13.5	47	8.6
1.018	11.5	18	13.3	48	8.4
1.019	11.3	19	13.2	49	8.3
1.020	11.0	20	13.0	50	8.1
1.021	10.7	21	12.9	51	7.9
1.022	10.5	22	12.7	52	7.8
1.023	10.2	23	12.5	53	7.6
1.024	10.0	24	12.4	54	7.4
1.025	9.7	25	12.2	55	7.3
1.026	9.4	26	12.0	56	7.1
1.027	9.2	27	11.9	57	7.0
1.028	8.9	28	11.7	58	6.8
1.029	8.6	29	11.5	59	6.6
1.030	8.4	30	11.4	60	6.5

TABL[illegible] ontinu

Hydrometer 151H		Hydrometer 152 H			
Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm
1.031	8.1				
1.032	7.8				
1.033	7.6				
1.034	7.3				
1.035	7.0				
1.036	6.8				
1.037	6.5				
1.038	6.2				

[A] Values of effective depth are calculated from the equation

$$L = L_1 + \tfrac{1}{2}\left[L_2 - \left(\frac{V_B}{A}\right)\right]$$

where:

L = effective depth, cm,

L_1 = distance along the stem of the hydrometer from the top of the bulb to the mark for a hydrometer reading, cm,

L_2 = overall length of the hydrometer bulb, cm,

V_B = volume of hydrometer bulb, cm^3, and

A = cross-sectional area of sedimentation cylinder, cm^2.

Values used in calculating the values in Table 2 are as follows:

For both hydrometers, 151H and 152H:

L_2 = 14.0 cm

V_B = 67.0 cm^3

A = 27.8 cm^2

For hydrometer 151H:

L_1 = 10.5 cm for a reading of 1.000

= 2.3 cm for a reading of 1.031

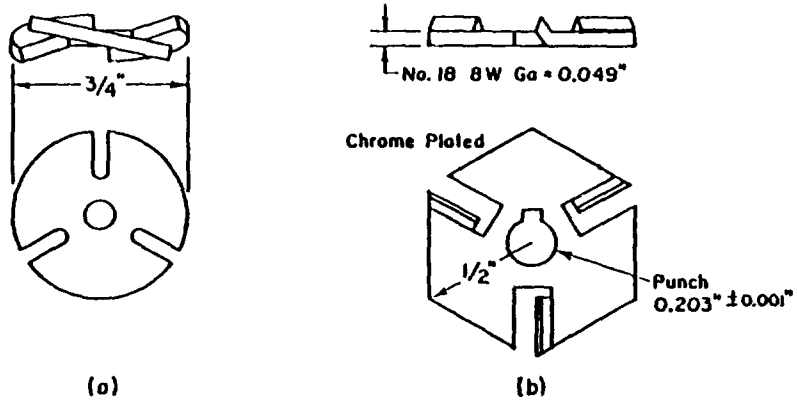
For hydrometer 152H:

L_1 = 10.5 cm for a reading of 0 g/litre

= 2.3 cm for a reading of 50 g/litre

TABLE 3 Values of A for Use in Equation for Computing Diameter of Particle in Hydrometer Analysis

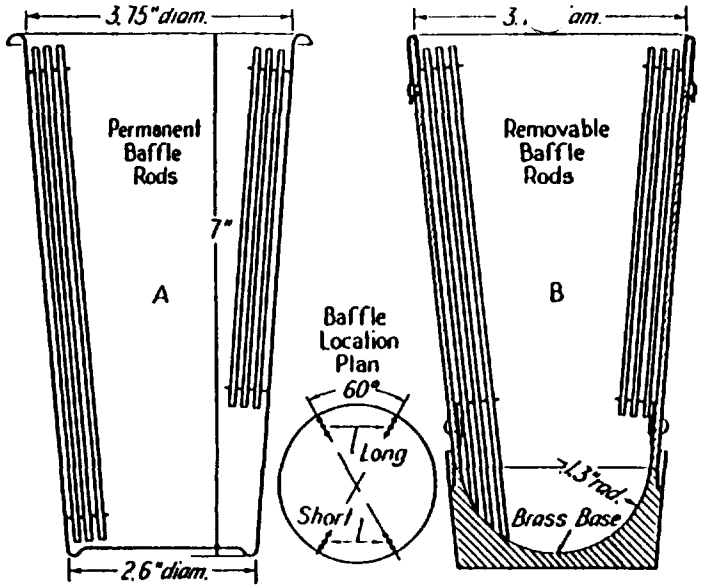
Temperature, °C	Specific Gravity of Soil Particles								
	2.45	2.50	2.55	2.60	2.65	2.70	2.75	2.80	2.85
16	0.01510	0.01505	0.01481	0.01457	0.01435	0.01414	0.01394	0.01374	0.01356
17	0.01511	0.01486	0.01462	0.01439	0.01417	0.01396	0.01376	0.01356	0.01338
18	0.01492	0.01467	0.01443	0.01421	0.01399	0.01378	0.01359	0.01339	0.01321
19	0.01474	0.01449	0.01425	0.01403	0.01382	0.01361	0.01342	0.1323	0.01305
20	0.01456	0.01431	0.01408	0.01386	0.01365	0.01344	0.01325	0.01307	0.01289
21	0.01438	0.01414	0.01391	0.01369	0.01348	0.01328	0.01309	0.01291	0.01273
22	0.01421	0.01397	0.01374	0.01353	0.01332	0.01312	0.01294	0.01276	0.01258
23	0.01404	0.01381	0.01358	0.01337	0.01317	0.01297	0.01279	0.01261	0.01243
24	0.01388	0.01365	0.01342	0.01321	0.01301	0.01282	0.01264	0.01246	0.01229
25	0.01372	0.01349	0.01327	0.01306	0.01286	0.01267	0.01249	0.01232	0.01215
26	0.01357	0.01334	0.01312	0.01291	0.01272	0.01253	0.01235	0.01218	0.01201
27	0.01342	0.01319	0.01297	0.01277	0.01258	0.01239	0.01221	0.01204	0.01188
28	0.01327	0.01304	0.01283	0.01264	0.01244	0.01255	0.01208	0.01191	0.01175
29	0.01312	0.01290	0.01269	0.01249	0.01230	0.01212	0.01195	0.01178	0.01162
30	0.01298	0.01276	0.01256	0.01236	0.01217	0.01199	0.01182	0.01165	0.01149



Metric Equivalents

in.	0.001	0.049	0.203	½	¾
mm	0.03	1.24	5.16	12.7	19.0

FIG. 1 Detail of Stirring Paddles



Metric Equivalents

in.	1.3	2.6	3.75
mm	33	66	95.2

FIG. 2 Dispersion Cups of Apparatus

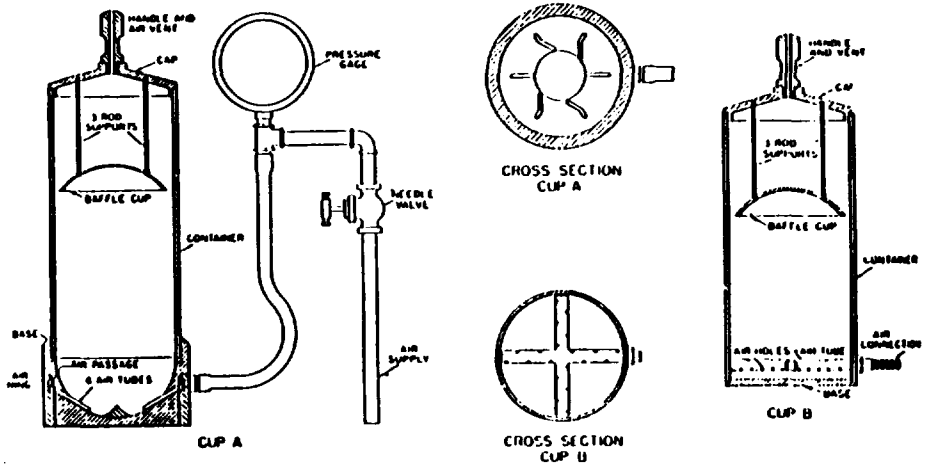
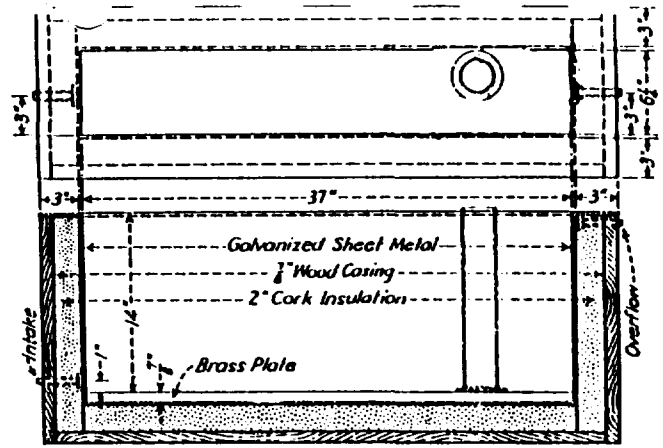


FIG. 3 Air-Jet Dispersion Cups of Apparatus B



Metric Equivalents

in.	⅜	1	3	6¼	14	37
mm	22.2	25.4	76.2	158.2	356	940

FIG. 4 Insulated Water Bath

PROCEDURES FOR SAMPLE COLLECTION, PRESERVATION, ENUMERATION AND IDENTIFICATION OF QAUATIC ORGANISMS

Prepared by

Peter G. Meier, Ph.D.
The University of Michigan

1.0 Phytoplankton are organisms of microscopic size that are incapable of sustained mobility against a current. They are designated as the primary producers of lentic system. These organisms will be collected with a 4-L Van Dorn water bottle. A composite over depth will be made and poured in a 1 L brown polybottle. If the sample is not analyzed immediately, it will be preserved with 5 mL of Lugols' solution.

Phytoplankton collected from the sites will be analyzed qualitatively and quantitatively. Part of the plankton sample will be removed and concentrated by centrifugation. After removal of the supernatant, the pellicle (residue) will be mixed with some water into a slurry. From this mixture replicate permanent diatom slides will be prepared using Hyrax as the mounting medium. These slides will be scanned under medium (450x) and high power (1000x) and the diatoms will be identified to the lowest possible taxa. Quantitative analysis for species composition will be carried out on unconcentrated samples employing the Palmer-Moloney nannoplankton cell. Two sub samples will be examined under 450x from each station. The data that will be generated will be presented in tabular form which will list divisions, orders, genera and species. Percentage composition of greens, bluegreens, diatoms and euglenoids will be presented. Composition will be evaluated from the water quality perspective.

2.0 Zooplankton are small microscopic to macroscopic animals that are capable of moving against a current. They are an important link in the food chain. Zooplankton may be divided into micro and macrofiltrators. Besides this feeding classification, members of this community have been employed as indicator organisms for categorizing the tropic status.

The zooplankton will be sampled with a #10 mesh (185 u) 0.5 M diameter net by making vertical hauls. The length of the tow will be dependent upon station depth. The content of the net will be washed down from the outside into a pint jar. Koechees solution (8% formalin-saturated sugar solution) in equal volume to that in the jar will be added for preservation.

Zooplankton samples contained in a pint jar will be analyzed quantitatively for species composition and concentration. Prior to any subsampling, the total volume of the liquid in the jar will be determined. From the information on the label in the jar, the amount of water that was filtered through the net will be calculated. From these two observations, the number of liters per mL of sample can be determined. The quantitative analysis of the zooplankton employs a dissecting scope (Baush and Lomb No. 7 Zoom), a Stempel pipette (volumetric 1 ml) and a series of spot or depression plates. The pint jar is placed on a magnetic stirrer and agitated with the stirring bar. While the mixing occurs, the Stempel pipette is used to obtain a subsample of 1 mL and deposited into a depression plate. Employing distilled water and an eye dropper, the 1 mL of sample is diluted to different depression areas to perit a population that can be counted easily under magnification. The counting technique is carried out three times on each zooplankton sample. The data generated is expressed in number of organisms per liter of water and presented in tabular form using appropriate taxonomic categories. Part of the zooplankton may be viewed under high magnification using a regular microscope to confirm species designation. Qualitative comparisons will be made between stations.

3.0 Benthic macroinvertebrates will be collected in duplicate from each station with an Ekman dredge. Contents of the sampler will be washed through a U.S. #30 mesh sieve and the retained portion will be transferred to a pint jar and the contents will be preserved with 90% ethanol.

The contents of the pint jar is poured into white enamel pans from which all the macroinvertebrates are handpicked and put in a small vial contained 70% ethanol. Using a dissecting microscope, the majority of organisms will be identified to genus and possibly species level. For their identification using up to 400x magnification, worms (Oligochaeta) will be mounted in Ammons lactophenol. Midges (Chiromonidae-Diptera) will be cleared using 10% KOH followed by 79% and 90% ethanol and then using Euparol Solution. Appropriate references will be employed to carry out this task. The qualitative analysis of the benthic organisms will be presented in tabular and graphic form. Organisms will be categorized in classes, orders, families, genera and species where practical and expressed in number per square meter.

4.0 Summary

In summary, it can be stated that an attempt will be made to use components of the aquatic community in the evaluation of water quality. If severe impacts results from the hazardous waste site on water quality than this should be reflected in the composition of aquatic flora and fauna.

YELLOW SPRINGS INSTRUMENT CO.
YELLOW SPRINGS, OHIO 45387

INSTRUCTIONS
FOR
YSI
MODEL 33
S-C-T
METER

TABLE OF CONTENTS

GENERAL DESCRIPTION

The YSI Model 33 S-C-T Meter is a portable, battery powered, transistorized instrument designed to accurately measure salinity, conductivity and temperature. It uses a probe consisting of a rugged, plastic conductivity cell and a precision YSI thermistor temperature sensor combined in a single probe.

Conductivity in umhos/cm is the measurement of electrical conductance a sample would have shown if measured between opposite faces of a 1 cm cube. Salinity is the number of grams of salt/kilogram of sample (‰ = parts per thousand). This measurement assumes the sample contains a "standard" sea water salt mixture. The sample temperature is measured in degrees Celsius.

Knowing temperature permits temperature correction of the conductivity and salinity measurements. Also, when just temperature and conductivity are known it is possible to calculate salinity, and when only temperature and salinity are known it is possible to calculate conductivity.

SPECIFICATIONS

Conductivity

Ranges:	0-500, 0-5,000, 0-50,000 umhos/cm with YSI 3300 Series Probes. (Note: The "umho" designations on the instrument are a shorthand form for "umho/cm".)
Accuracy:	± 2.5% max. error at 500, 5,000 and 50,000 plus probe ± 3.0% max. error at 250, 2,500 and 25,000 plus probe See Error Section

Readability:	2.5 umhos/cm on 500 umho/cm range 25 umhos/cm on 5000 umho/cm range 250 umhos/cm on 50000 umho/cm range

Salinity

Range:	0-40 ‰ (parts per thousand) over temperature range -2 to +45°C.
Accuracy:	Above 4°C, ± 0.9 ‰ at 40 ‰ and ± 0.7 ‰ at 20 ‰ plus conductivity probe. Below 4°C, ±1.1 ‰ at 40 ‰ and ± 0.9 ‰ at 20 ‰ plus conductivity probe. See Error Section.
Readability:	0.2 ‰ on 0-40 ‰ range

Temperature

Range:	+ 50 to -2°C
Accuracy:	± 0.1°C at -2°C, ± 0.6°C at 45°C plus probe. See Error Section.
Readability:	± 0.15°C at -2°C to ± 0.37°C at 45°C

Power Supply	Two D size alkaline batteries, Eveready E95 or equivalent, provide approximately 200 hrs. of operation.

Probe	YSI 330C Series Conductivity/Temperature Probe Nominal Probe Constant: K =5
Accuracy:	Max. error ±2% of reading for conductivity and salinity. Max. error of ±0.1°C for temperature.
Instrument	
Ambient Range:	Satisfactory operation -5 to +45°C. A maximum error of ± 0.1% of the reading per °C change in instrument temperature can occur. This error is negligible if the instrument is readjusted to redline for each reading.

OPERATION PROCEDURE

1. **Setup**
   - (a) Adjust meter zero (if necessary) by turning the bakelite screw on the meter face so that the meter needle coincides with the zero on the conductivity (umhos/ cm) scale.
   - (b) Calibrate the meter by turning the switch to redline and adjusting the meter needle with the redline control to the red line on the scale. If this cannot be accomplished, replace the batteries.
   - (c) Plug the probe into the probe jack on the side of the instrument.
   - (d) Put the probe in the solution to be measured (See Probe Use).

2. **Temperature**

   Set the switch to temperature. Read the temperature on the bottom scale of the meter in degrees Celsius. Allow time for the probe temperature to come to equilibrium with that of the water before reading.

3. **Salinity**
   - (a) Transfer the temperature reading from Step 2 to the temperature knob on the instrument.
   - (b) Switch the instrument to the SALINITY position and read salinity on the red 0-40 ‰ meter range.
   - (c) Depress the CELL TEST button. The meter reading should fall less than 2%; if greater, the probe is fouled and the measurement is in error. Clean the probe and re-measure.

4. **Conductance**
   - (a) Switch the meter to the X100 umhos/cm range. If the reading is below 50 on the 0-500 meter scale, switch to the next lower range (X10 umhos/cm). If the reading is still below 50, switch to the next lower range (X1 umhos/cm). Read the meter scale and multiply that reading by the range (X100, etc.) The answer is the reading in umhos/cm.

Example:	Meter Reading	247	
	Reading	X10	
	Answer	2470 umhos/cm	or
		.00247 mhos/cm	

(b) When measuring on the X100 and X10 ranges, depress the CELL TEST button. The meter reading should fall less than 2%; if greater, the probe is fouled and the measurement is in error. Clean the probe and re-measure.

NOTE: The CELL TEST does not function on the X1 range.

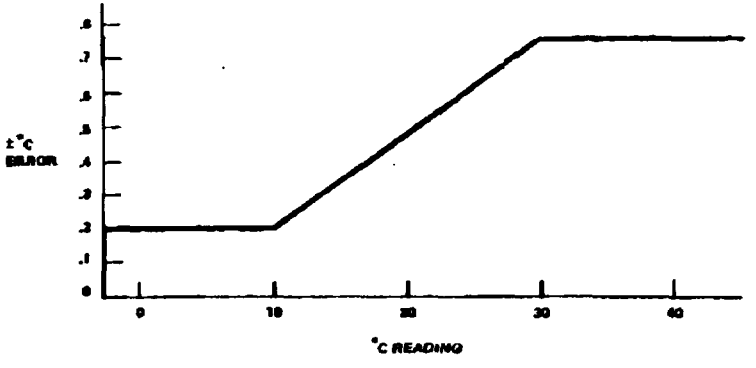
5. Error

The maximum error in a reading can be calculated by using the graphs in the following sections.

(1) Temperature

The temperature scale is designed to give the minimum salinity error when the temperature readings are used to compensate salinity measurements.

Figure 1 shows total error for probe and instrument versus °C reading.



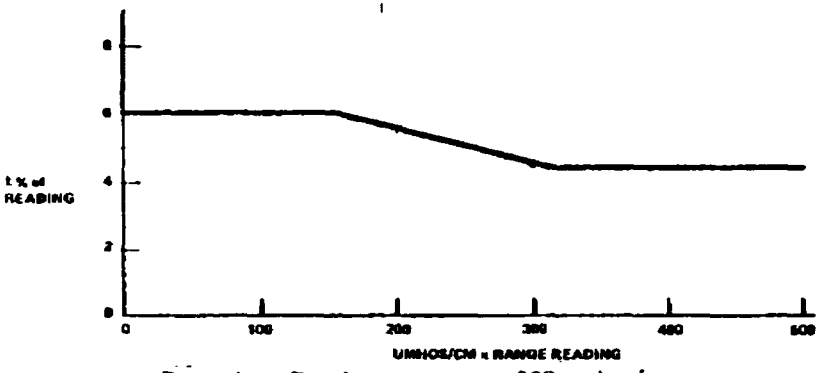
Example: Reading 25°C

Error .6°C

Accuracy 25°C ± 0.6°C for probe and instrument combined

(2) Conductivity

Figure 2 shows the worst case conductivity error as a function of the conductivity reading for the probe and instrument combined.



Example: Reading 360 umhos/cm

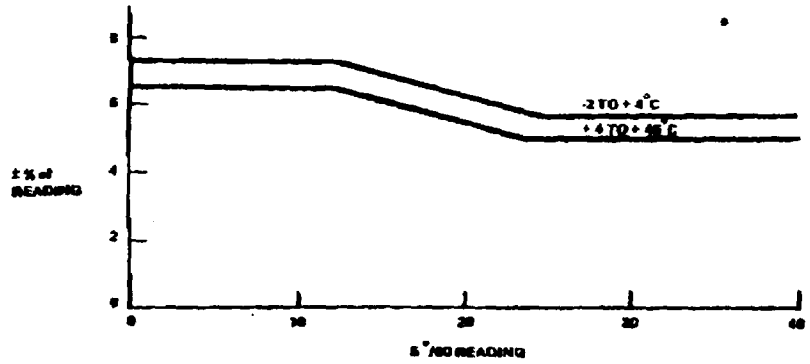
Range X10

% Reading Error ± 4.5%

Accuracy 3600 ± 162 umhos/cm for probe and instrument

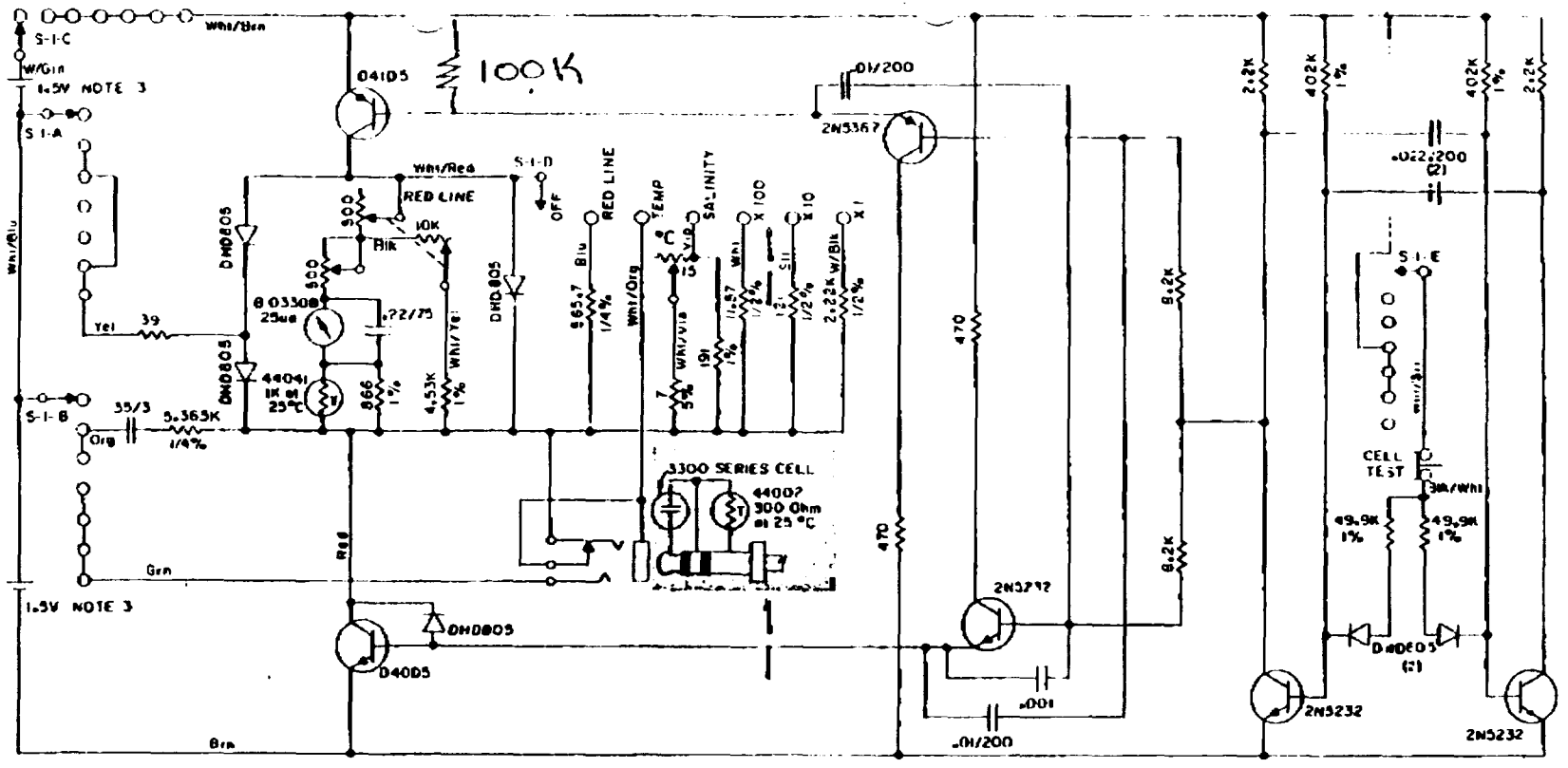
(3) Salinity

The salinity readings are a function of temperature and conductivity, therefore the accuracy is a function of both. The temperature scale and temperature control have been designed to minimize the temperature error contribution to the salinity error. The error shown in Figure 3 is the total of the temperature and conductivity probe, the temperature scale and the salinity scale errors.



Example: Reading 10 part/thousand, @ 10°C

% of Reading Error	6.5%
Accuracy	10 ‰ ± 0.65 ‰ for all errors, combined worst case.



NOTE:

1. Resistance values in ohms, K=1,000; resistors are ¼W, 10% unless otherwise specified.
2. The values shown on the schematic may differ from those in the instrument; of no, either value can be used for replacement purposes.
3. Battery is "D" size, alkaline only, Eveready E-95 or equal.

YSI MODEL 33 B-03528-A

CIRCUIT DESCRIPTION, MAINTENANCE AND CALIBRATION

1. Description

The circuit is composed of two parts; a multivibrator and switching transistors. The multivibrator produces a square waveform voltage. The square wave is applied to two switching transistors. They alternately apply two batteries of opposite polarity to the probe thus providing AC power which minimizes polarization effects. The meter is in series with one battery and measures the current from it. The current from the battery is proportional to the conductance of the cell. Salinity is measured in a special range conductivity circuit which includes a customer-adjusted temperature compensator. In the temperature, redline and X1 positions the multivibrator operated at 100 Hz. In the salinity, X100 and X10 positions the multivibrator operates at 600 Hz and on these ranges pushing the CELL TEST button drops the frequency to 100 Hz allowing the operator to judge the degree of probe polarization.

2. Maintenance

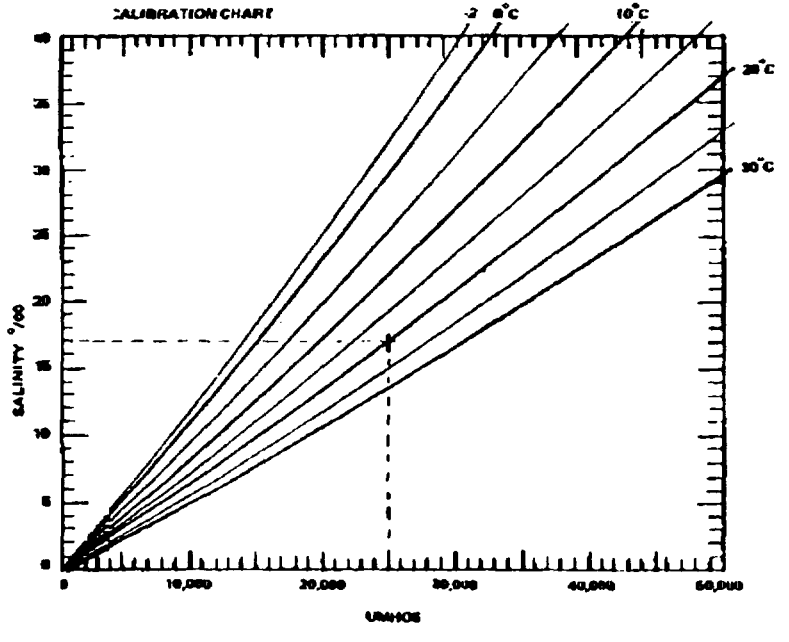
The only maintenance required is battery replacement. Two "D" size alkaline flashlight cells, such as Eveready E95 or equivalent batteries will provide 200 hrs. of operation. Accuracy will not be maintained if zinc-carbon "D" cells are used. Battery replacement is indicated when the redline adjustment cannot be accomplished.
Replace batteries every six months to reduce the danger of corrosion due to leaky batteries. To replace batteries, remove the six screws from the bottom plate. The battery holders are color coded. The Positive (+ button) end must go on red.

3. Calibration

It is possible for the temperature knob to become loose or slip from its normal position. In an emergency the dial can be re-positioned. It must be emphasized that this is an emergency

procedure only, and that the instrument should be returned to the factory for proper recalibration at the earliest opportunity.

(a) Read the temperature and conductance of the solution. Determine the salinity of the solution by running a line vertically on the graph from this conductance value until it intersects the appropriate °C line (interpolate as required for



temperatures between the given °C lines). From this intersection extend a line horizontally to the edge of the graph. This determines the salinity for this sample.
Example: 25000 umhos and 20°C gives a salinity of 17.

(b) Remove the °C knob, switch to SALINITY, and turn the control shaft until the meter needle indicates the salinity value determined in Step (a). In the example given, the value is 17.

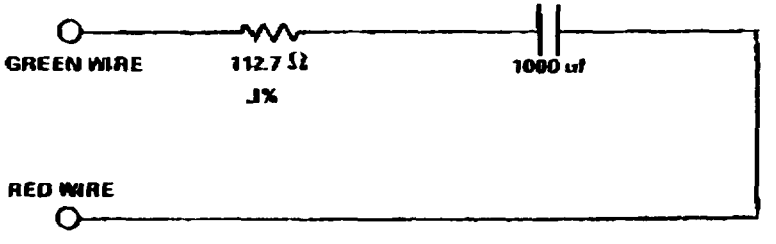
(c) Switch to TEMPERATURE (Note: This temperature reading must be the same as Step (a); if not, begin again at Step (a).) Place the knob on the control shaft (without turning the control shaft) with the knob pointer at the same temperature as the meter reading and tighten both set screws securely.

At earliest opportunity recalibrate using the following procedure or return the instrument to factory for service.

(a) Set the instrument for a salinity measurement as normal.

(b) Substitute a 1000 uf capacitor and 112.7 ohm 0.1% tolerance resistor for the probe.

Connect the resistor and capacitor between the green wire and red wire on the jack connections inside the instrument.



(c) Turn the temperature dial until the meter reads redline. Now install the temperature knob with the arrow at 25°C. This is a temporary calibration only. Return the instrument to the factory for proper recalibration.

PROBE

1. Description of YSI 3300 Series Conductivity/Temperature Probe

The YSI 3300 Series Conductivity Probes are designed for field/portability embodying construction and design for rugged, accurate service.

Each probe features a built-in cell constant of 5.00 ± 0.1, a precision YSI thermistor temperature sensor of ± 0.1°C accuracy, and a low capacitance cable assembly terminating in a three terminal 0.25 dia. phone type connector.

The 3310 has a 10 ft. cable and the 3311 is a 50 ft. version. Other lengths are available on special order.

The probe has a rigid P.V.C. body, platinized pure nickel electrodes, and a chrome-vinyl jacket cable, providing resistance to a wide range of water-borne substances.

2. Maintenance

(a) Cleaning

When the cell test indicates low readings the probable cause is dirty electrodes. Hard water deposits, oils and organic matter are the most likely contaminants.

For convenient normal cleaning soak the electrodes for 5 minutes with a locally available bathroom tile cleaning preparation such as: Dow Chemical "Bathroom Cleaner"; Horizon Industries "Rally, Tile, Porcelain, and Chrome Cleaner"; Johnson Wax "Envy, Instant

Cleaner"; or Lysol Brand "Basin, Tub, Tile Cleaner."

For stronger cleaning a 5 minute soak in a solution made of 10 parts distilled water, 10 parts isopropyl alcohol and 1 part HCl can be used.

Always rinse the probe after cleaning and before storage.

CAUTION: Do not touch the electrodes inside the probe. Platinum black is soft and can be scraped off.

If cleaning does not restore the probe performance, re-platinizing is required.

(b) Re-Platinizing

Equipment Required –

(1) YSI #3140 Platinizing Solution, 2 fl. oz. (3% Platinum Chloride dissolved in .025% lead acetate solution).
(2) YSI Model 33 S-C-T Meter.
(3) 50 ml glass beaker or equivalent bottle.
(4) Distilled water.

Procedure –

(1) Clean the probe as in Section (a) – either method.
(2) Place the cell in the beaker and add sufficient solution to cover the electrodes. Do not cover the top of the probe.
(3) Plug the probe into the Model 33, switch to the X100 range to platinize the electrode. Move the probe slightly to obtain the highest meter reading and continue platinizing for the approximate time shown below:

Meter Reading (umhos)	Time (minutes)
30,000	5
25,000	6
20,000	8
15,000	11
10,000	16

(4) After the elapsed time remove the probe and rinse in fresh water.

(5) Return the solution to its container. 2 oz. of solution should be suificient for 50 treatments.

3. Probe Use

(a) Obstructions near the probe can disturb readings. At least two inches of clearance must be allowed from non-metallic underwater objects. Metallic objects such as piers or weights should be kept at least 6 inches from the probe.

(b) Weights are attached to the cable of the YSI 3310 and 3311 Probes. The YSI 3327 Weights are supplied in pairs with a total weight of 4 ounces per pair. Should it become necessary to add more weight to overcome water currents, we suggest limiting the total weight to two pounds (8 pairs). For weights in excess of two pounds use an independent suspension cable. In either case, weights must be kept at least 6 inches away from the probe.

(c) Agitations

Gentle raising and lowering of the probe several times during a measurement insures flow of specimen solution through the probe and improves the time response of the temperature sensor.

4. Cell Calibration & Standard Solutions

The YSI #3300 Series Cells are calibrated to absolute accuracy of ± 1-1/2% based on a standard solution. Since the literature on conductivity does not indicate a consistently accepted standardization methods, we have chosen the .01 demal KCl solution method as determined by Jones and Bradshaw in 1937 as our standard. Recent textbooks, as well as the ASTM standards, concur with this choice.

The solution is prepared by diluting .745 grams of pure dry KC1 with distilled water until the solution is 1 kilogram. The table below

shows the values of conductivity this solution would have if the distilled water were non-conductive. However, since even high purity distilled water is slightly conductive, the measured conductivity will be higher by an amount equal to the water's conductivity.

Temperature °C	Conductivity (Absolute Micromhos/cm³)
15	1141.5
16	1167.5
17	1193.6
18	1219.9
19	1246.4
20	1273.0
21	1299.7
22	1326.6
23	1353.6
24	1380.8
25	1408.1
26	1436.5
27	1463.2
28	1490.9
29	1518.7
30	1546.7

The operator may use the standard solution and the table to check accuracy of a cell's constant or to determine an unknown constant. The formula is shown below:

$$K = \frac{R(C_1 + C_2)}{10^6}$$

where: K = Cell Constant
R = measured resistance in ohms
C_1 = conductivity in absolute micromhos
C_2 = conductivity in absolute micromhos of the distilled water used in making solution

R, C_1 and C_2 must either be determined at the same temperature or corrected to the same temperature to make the equation valid.

Note: For further information on conductivity and the above standard information, refer to ASTM Standards Part 23 – Standard Methods of Test for Electrical Conductivity, or Water and Industrial Waste Water – ASTM Designation D1125-64.

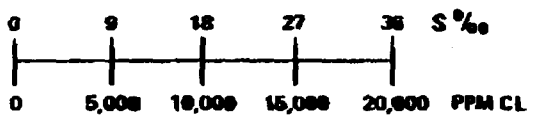
YSI MODEL 33 USED WITH YSI 51A or 54 OXYGEN METER

If the Model 33 salinity measurement is to be used for salinity correction on the 51A, the reading should be converted to Chlorosity. The formula is:

$$\text{PPM Chlorosity} = \frac{\text{Salinity } ‰ - 0.03}{1.8} \times 10^3$$

For these instruments the 0.03 can be neglected so the equation simplifies to:

$$\text{PPMCl} = \frac{S\ ‰}{1.8} \times 10^3$$



REPAIR FACILITIES

If you are experiencing difficulty with a YSI product, it may be returned to the YSI Customer Service Department for repair, even if the guarantee has expired. YSI maintains complete facilities for prompt servicing of all YSI products.

GUARANTEE

The Model 33 S-C-T Meter carries a one year unconditional guarantee on all workmanship and components. Damage through accident, misuse, or tampering will be repaired at a nominal charge when the instrument is returned to our plant. Cells are similarly guaranteed.

Note: In communications regarding this instrument, please mention model number and serial number.

YELLOW SPRINGS INSTRUMENT CO.
YELLOW SPRINGS, OHIO 45387

INSTRUCTIONS
FOR
YSI
MODEL 57
DISSOLVED OXYGEN
METER

DO NOT LOSE!!

INSTRUCTIONS FOR YSI MODEL 57 OXYGEN METER

OUTLINE OF OPERATION

(For detailed description see — Setup for Operation)

1. With the instrument OFF check mechanical ZERO.
2. Switch instrument to RED LINE and adjust meter to red line.
3. Prepare the oxygen probe for use, connect to instrument and wait 15 minutes for probe to polarize.
4. Switch to ZERO and adjust to zero position.
5. Place probe in calibration medium.
6. Adjust SALINITY control to zero.
7. Switch to TEMPERATURE and read temperature when meter is steady.
8. Switch to desired dissolved oxygen range, 0-5, 0-10 or 0-20 and with the CALIBRATE control adjust meter to the correct calibration value. (See TABLES I & II)
9. Place probe in sample solution, allow it to come to temperature and stir.
10. Adjust salinity control, if necessary.
11. Read dissolved oxygen while stirring sample.
12. We recommend instrument be left on between measurements to avoid necessity for repolarizing probe.
13. Repeat 9, 10, & 11 for subsequent measurements.

TABLE OF CONTENTS

GENERAL DESCRIPTION

The YSI Model 57 Dissolved Oxygen Meter is an instrument for the measurement of oxygen dissolved in fresh water or sea water. The instrument indicates dissolved oxygen in parts per million on one of three ranges, 0-5, 0-10 or 0-20 ppm. All ranges are automatically temperature compensated and manually salinity compensated. The probe uses a Clark-type membrane covered polarographic sensing element. Two precision thermistors are built into the sensor to sense and compensate for temperature changes.

The Model 57, designed for field operation, has a durable gasketed case, metal meter cover, shaft-sealed controls, and water tight electrical connectors.

SPECIFICATIONS

Oxygen Measurement

Ranges:	0-20, 0-10, 0-5 ppm
Accuracy:	±1% or 0.1 ppm (whichever is larger)
Readability:	0.5% of range

Temperature Reading

Range:	-5° to +45°C
Accuracy:	±0.5°C plus probe, which is ±0.1°C
Readability:	0.3°C

Temperature Compensation ±1% of D.O. reading for measurements made within ±5°C of calibration temperature.
±3% of D.O. reading for fresh water measurements when temperature varies from calibration temperature over the entire -5° to +45°C span.

Salinity Compensation

Range:	0 – 40 ppt
Accuracy:	±2.5% of DO reading for 40 ppt change
Settability:	1 ppt

Oxygen Probe
Accuracy: Included in above statements.

System Response Time Typical response for temperature and DO readings is 90% in 10 sec. DO response at low temperature and low DO is typically 90% in 30 sec. The YSI 5937 High Sensitivity Membrane can be used to improve response at low temperature and low DO concentration. If total response time under any operating conditions exceeds two minutes, probe service is indicated.

Operating Temperature Range Instrument operating range -5° to +45°C. Large ambient temperature changes will result in 2% loss of accuracy unless Red Line and Zero are re-set.

Recorder Output: 125 mV, 11 mV. Recorder requires 50,000 ohms input impedance.

Power Supply: The Model 57 is powered by two disposable "C" size carbon zinc batteries, providing approximately 1000 hour operation.

Accessories

5718 Oxygen Temperature Probe with 10' lead for field use.

5719 Oxygen Temperature Probe with 50' lead and pressure compensating system for field use. Longer leads can be provided.

5034 Service Kit contains KCl, membranes and other material for servicing probes.

5952 Carrying Case of plastic and aluminum for carrying instrument, probes and accessories.

5791 Submersible Stirrer automatically stirs the sample when measuring in large containers or bodies of water.

5721 Battery and Charger Pack power supply for the submersible stirrer.

5734 Adaptor makes it possible to use YSI 5400 Series Probes with the YSI Model 57 Dissolved Oxygen Meter.

5937 High Sensitivity Membrane improves response when working at low temperatures and with low DO concentrations.

5075 Calibration Chamber helps obtain maximum accuracy when air calibrating in the field.

OPERATING PROCEDURE

I Probe Preparation

All YSI 5700 Series Oxygen Probes have similar sensors and should be cared for in the same manner. They are precision devices relying on good treatment if high accuracy measurements are to be obtained.

The YSI 5034 Service Kit contains the necessary material, except for distilled water, to put the system in operation. The procedure for preparing the probe is as follows:

1. Add *distilled* water to the KCl crystals to fill the bottle. Dissolve the crystals completely.
2. Transfer a part of the KCl solution to the eyedropper bottle.
3. Remove the sensor guard from the probe.
4. Remove the "O" ring and old membrane.
5. Inspect the cathode surface and central anode well of the sensor for salt crystals or foreign matter. Flush the probe with KCl solution or distilled water to clean.
6. Lift a membrane from the membrane pack and place it in easy reach.
7. To fill the probe and install the new membrane, follow Steps A through F, referring to the drawings in Figure 1.
   A) Grasp threaded end of probe between thumb and forefinger. Secure one end of membrane under thumb. Use eyedropper to fill central well of probe with KCl solution.

      The pressure compensating tube of the 5719 probe must be completely full with solution. This is best done by slipping the piece of plastic tubing supplied with the probe over the end of the probe and filling it to the top with solution. Pump the tube with a flat object, such as a match book cover or credit card, until all bubbles are worked out and the tube is

full. Remove the large tube

When finished with filling the probe, a large meniscus of solution should completely cover the gold cathode.

B) With thumb and forefinger of your other hand, grasp the free end of the membrane.

C) Using a continuous motion *stretch* the membrane *up, over,* and *down* the other side of the sensor. Stretching forms the membrane to the contour of the probe.

D) Secure the end of the membrane under the forefinger of the hand holding the probe.

E) Roll the "O" ring over the end of the probe. There should be no wrinkles or trapped air bubbles in the probe. Some wrinkles may be removed by tugging on the sides of the membrane beyond the "O" ring.

F) Trim off excess membrane with scissors or a sharp knife. The stainless steel temperature sensor should not be covered by excess membrane.

8. After installing the new membrane, shake off excess KCl and reinstall the sensor guard.

NOTES: 1) The probe is supplied with a weight attached to the cable. Should it become necessary to add more weight we suggest limiting the total weight to 2 pounds. For weights in excess of two pounds, a separate suspension cable should be used.

2) The small plastic bottle, YSI #5033, in the Service Kit is convenient for storing probes. Place a small, moist towel or sponge in the bottle and slip the end of the probe inside the bottle. The moisture will prevent the probe from drying out.

3) YSI 5718 and 5719 Probes use the YSI #110, 3/8" I.D. X 9/16" O.D. X 3/32" wall, "O" ring.

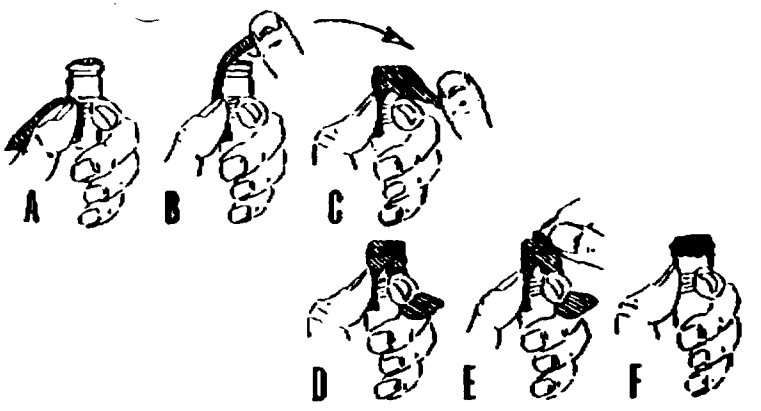


Figure 1

II Setup for Operation

1. Attach the prepared probe to the PROBE connector of the instrument and turn the retaining ring finger tight.
2. Place the instrument in the intended operating position – vertical, tilted, or on its back – with the instrument OFF. Adjust the meter pointer to zero with the black screw in the center of the meter panel. Readjustment may be necessary when the instrument position is changed.
3. Switch to RED LINE and adjust the RED LINE knob until the meter needle aligns with the red mark at the 31°C position.
4. Before calibrating allow 15 or 20 minutes for the probe to polarize. Repolarize whenever the instrument has been OFF or the probe has been disconnected.

III Calibration Procedures

The operator has a choice of three calibration procedures. These include Winkler titration as a reference, using saturated water as a reference, or using a gas with known oxygen content, such as air, as a reference. Experience has shown that air calibration is quite reliable and far simpler than the other techniques.

A. Winkler Titration

1. Draw a volume of water from a common source and divide into four samples. Determine the oxygen in three samples using the Winkler titration technique and average the three values. If one of the values differs from the other two by more than 0.5 ppm, discard that value and average the remaining two.
2. Place the oxygen probe in the fourth sample and begin stirring.
3. Set the SALINITY control to zero or the appropriate salinity value of the sample.
4. Adjust the CALIBRATION control to the average value determined in Step 1. Allow the probe to remain in the sample for at least two minutes before setting the calibration value, and leave in the sample for an additional two minutes to verify calibration stability. Readjust if necessary.

B. Saturated Water Technique

1. Saturate 300-500 cc of water by aerating or stirring for at least 15 minutes at a relatively constant temperature.
2. Place the probe in the sample and switch to TEMPERATURE. Refer to TABLE I for the ppm value corresponding to this temperature.

3. Determine local altitude or the "true" atmospheric pressure (note that "true" atmospheric pressure is as read on a mercury barometer. Weather Bureau reporting of atmospheric pressure is corrected to sea level). From TABLE II determine the correction factor for your pressure or altitude.
4. Multiply the ppm value from TABLE I by the correction factor from TABLE II to determine the corrected calibration value for your conditions.

   Example:

   Assume temperature = 21°C and altitude = 1000 feet

   From TABLE I the calibration value for 21°C is 9.0 ppm

   From TABLE II the correction factor for 1000 ft. is about 0.96

   The corrected calibration value is 9.0 ppm X 0.96 = 8.6 ppm.
5. Switch to an appropriate ppm range, set the SALINITY knob to zero and adjust the CALIBRATE knob while stirring until the meter reads the corrected calibration value from Step 4. Leave the probe in the sample for two minutes to verify calibration stability. Readjust if necessary.

C. Air Calibration

1. Place the probe in moist air by wrapping loosely in a damp cloth, taking care that the cloth does not touch the membrane. If the YSI 5075 Calibration Chamber is available, refer to V Calibration Chamber. Wait approximately 10 minutes for temperature stabilization.
2. Switch to TEMPERATURE and read. Refer to TABLE I – Solubility of Oxygen in Water, and determine calibration value.

3. Determine altitude or atmospheric correction factor from TABLE II.
4. Multiply the calibration value from TABLE I by the correction factor from TABLE II

   Example:

   Assume temperature = 21°C and altitude = 1000 feet.
   From TABLE I the calibration value for 21°C is 9.0 ppm
   From TABLE II the correction factor for 1000 ft. is about 0.96.
   Therefore, the corrected calibration value is 9.0 ppm X 0.96 = 8.6 ppm.
5. Switch to the appropriate ppm range, set the SALINITY knob to zero and adjust the CALIBRATE knob until the meter reads the corrected calibration value from Step 4. Wait two minutes to verify calibration stability. Readjust if necessary.

The probe is now calibrated and should hold this calibration value for many measurements. Calibration can be disturbed by physical shock, touching the membrane or drying out of the electrolyte. Check calibration after each series of measurements and in time you will develop a realistic schedule for recalibration. For best results when not in use, store the probe in the plastic bottle provided with the Service Kit to help prevent the electrolyte from drying out.

IV Dissolved Oxygen Measurement

1. Place the calibrated and polarized probe in the water and switch the STIRRER knob ON. Allow about 30 seconds for the probe to come to equilibrium with the water. If the YSI 5731 Submersible Stirrer is not used, provide manual stirring by raising and lowering the probe about 1 ft. per second. If the YSI 5075 Calibration Chamber is used, the entire chamber may be waved through the water at 2-3 ft. per second.
2. Adjust the SALINITY knob to the salinity of the sample.
3. Switch to the appropriate ppm range and read DO directly.

V Calibration Chamber (Figure 2)

The 5075 Calibration Chamber helps obtain maximum accuracy when air calibrating in the field and is also a useful tool when measuring in shallow water. It consists of a 4-1/2 ft. stainless steel tube (1) attached to the calibration chamber (5) and the measuring ring (7). For calibration insert the solid rubber stopper (6) into the bottom of the calibration chamber (5). Push the probe (4) through the hollow rubber stopper (3) as shown in Detail A. For maximum accuracy wet the inside of the calibration chamber (5) with fresh water. This creates a 100% relative humidity environment for calibration. Insert the probe-stopper assembly in the top of the calibration chamber.

During calibration hold the calibration chamber under water and calibrate as described in the Air Calibration procedure. Keep the handle above the water at all times. After calibration the chamber can be used as a measuring aid by removing the probe-stopper assembly from the calibration chamber (5) and placing it in measuring ring (7). (See Detail C). Slowly stir the water with the wand when measuring.

VI Submersible Stirrer and Power Supply

The YSI 5791 Submersible Stirrer automatically stirs the sample when measuring in large containers or bodies of water, and is particularly useful for short term monitoring. Either the YSI 5718 or 5719 Oxygen Temperature Probe is screwed into the top of the stirrer and the assembly lowered into the sample. (See Figure 3) Standard lead length is 50', but leads to 250' can be provided.

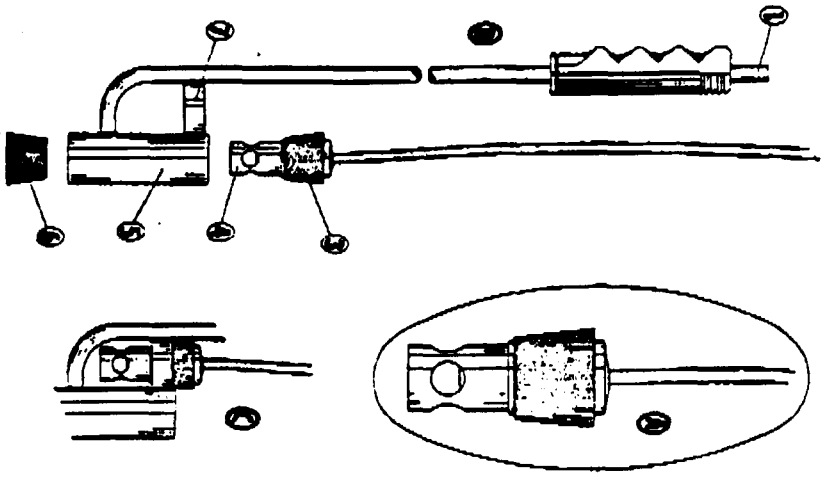
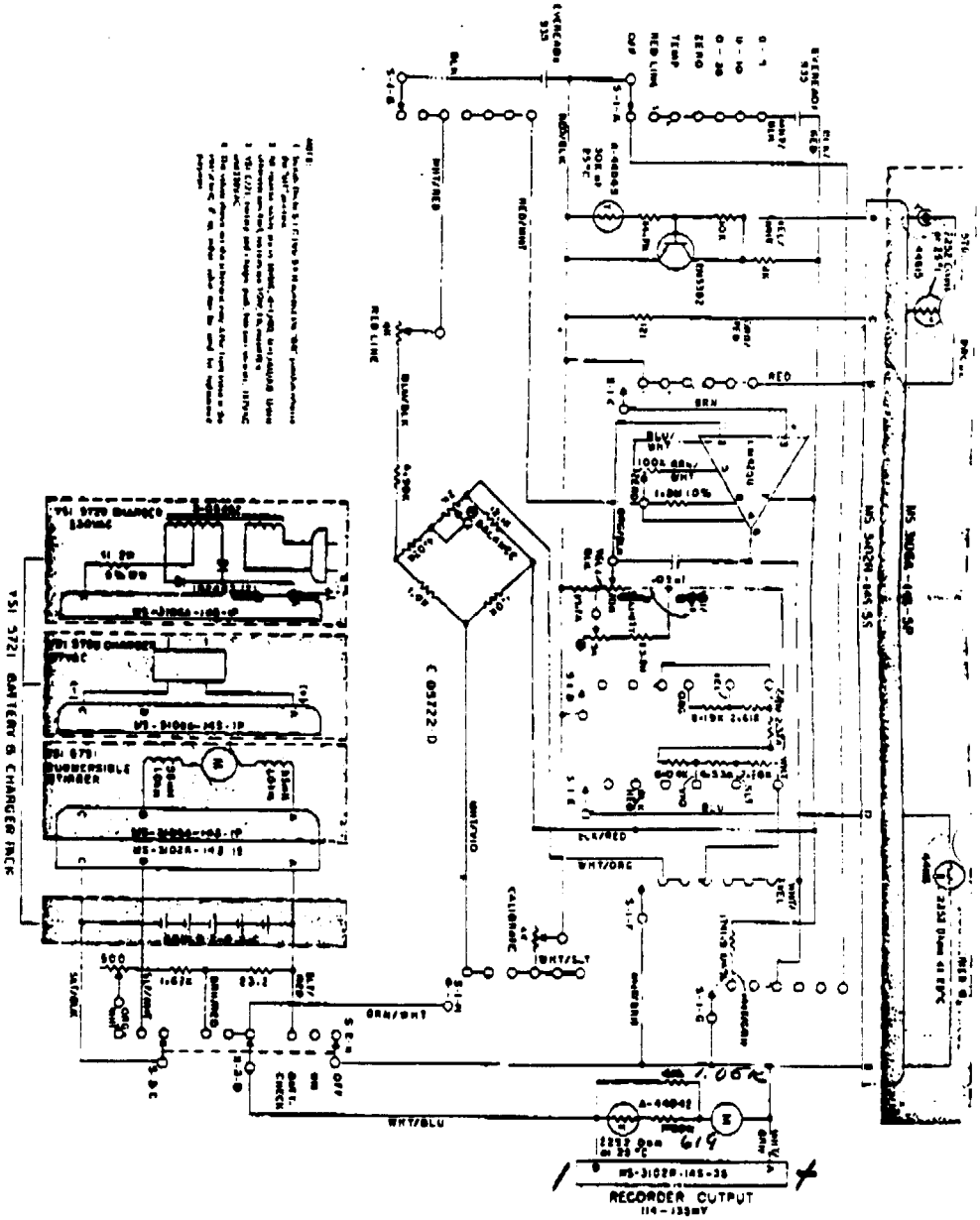


Figure 2


RECORDER OUTPUT
114 - 133mV
WHT/BLU
BRN/WHT
WHT/ORG
BLK/RED
WHT/RED
RED
BRN
YSI 5721 BATTERY & CHARGER PACK

VII Calibration Tables I & II

TABLE I – Solubility of Oxygen in Fresh Water

This table shows the amount of oxygen in ppm that is dissolved in air saturated fresh water at sea level (or 760 mmHg atmospheric pressure) as temperature varies from 0° to 45°C.

Temperature °C	PPM Dissolved Oxygen	Temperature °C	PPM Dissolved Oxygen
0	14.6	23	8.7
1	14.2	24	8.5
2	13.9	25	8.4
3	13.5	26	8.2
4	13.1	27	8.1
5	12.8	28	7.9
6	12.5	29	7.8
7	12.2	30	7.7
8	11.9	31	7.5
9	11.6	32	7.4
10	11.3	33	7.3
11	11.0	34	7.2
12	10.8	35	7.1
13	10.6	36	7.0
14	10.4	37	6.8
15	10.2	38	6.7
16	9.9	39	6.6
17	9.7	40	6.5
18	9.5	41	6.4
19	9.4	42	6.3
20	9.2	43	6.2
21	9.0	44	6.1
22	8.8	45	6.0

TABLE II – Correction Factor

This table shows the correction factor that should be used to correct the calibration value for the effects of atmospheric pressure or altitude. Find true atmospheric pressure in the left hand column and read across to the right hand column to determine the correction factor. (Note that "true" atmospheric pressure is as read on a barometer. Weather Bureau reporting of atmospheric pressure is corrected to sea level.) If atmospheric pressure is unknown, the local altitude may be substituted. Select the altitude in the center column and read across to the right hand column for the correction factor.

Atmospheric Pressure mmHg	or	Equivalent Altitude Ft.	=	Correction Factor
775		-540		1.02
760		0		1.00
745		542		.98
730		1094		.96
714		1688		.94
699		2274		.92
694		2864		.90
669		3466		.88
654		4082		.86
638		4756		.84
623		5403		.82
608		6065		.80
593		6744		.78
578		7440		.76
562		8204		.74
547		8939		.72
532		9694		.70
517		10472		.68
502		11273		.66

DISCUSSION OF MEASUREMENT ERRORS

There are three basic types of errors which can occur. Type I errors are related to limitations of the instrument design and tolerances of the instrument components. These are chiefly the meter linearity and resistor tolerances. Type II errors are due to basic probe accuracy tolerances, chiefly background signal, probe linearity, and variations in membrane temperature coefficient. Type III errors are related to the operator's ability to determine the conditions at the time of calibration. If calibration is performed against more accurately known conditions, Type III errors are appropriately reduced.

Individual Sources of Error

This description of sources of error can be used to attach a confidence to any particular reading of dissolved oxygen. The particular example given is for a near extreme set of conditions. As a generality, overall error is diminished when the probe and instrument are calibrated under conditions of temperature and dissolved oxygen which closely match the sample temperature and dissolved oxygen.

Type I

A – is the error due to the meter linearity.
Error = ±1% of full scale of the measurement range.

B – is the error due to tolerances in the instrument when transferring a reading from one range to another.
Error = ±1% of the meter reading if the reading is taken on a range one range away from the calibration range.
Error = ±2% of the meter reading if the reading is taken on a range two ranges away from the calibration range.

C – is the error due to the design and components of the instrument salinity compensation circuit.

$$\text{Error} = \pm 2.5\% \text{ of the meter reading} \times \frac{\text{sample salinity ppt}}{40 \text{ ppt salinity}}$$

Type II

A – errors are due to probe background current.

$$\text{Error} = 0.5\% \left(1 - \frac{\text{meter reading ppm}}{\text{Calib. value}}\right) \times \text{calib. value.}$$

B – errors are due to the probe non-linearity
Error = ±0.3% of reading.

C – error is caused by variability in the probe membrane temperature coefficient.
Error = zero if readings are taken at the calibration temperature.
Error = ±1% of meter reading if readings are taken with 5°C of the calibration temperature.
Error = ±3% of meter reading all other conditions.

Type III

A – errors are due to the accuracy of the instrument thermometer when used to measure the exact probe temperature during calibration.
Error = ±1.5% of reading.

B – errors are due to the assumption of mean barometric pressure. Daily variation is usually less than 1.7%
Error = ±1.7% of reading.

C – errors are included assuming an ability to estimate altitude to within ±500 ft. when computing the altitude correction factor.
Error = ±1.8% of reading.

D – errors consider the possibility of only 50% relative humidity when calibrating the probe. If the actual relative humidity is 50% instead of 100% the errors will be as follows:

Calibration Temperature ±C	Error in percent of reading
0	(-) 0.3
10	(-) 0.6
20	(-)1.15
30	(-)2.11
40	(-)3.60

Example of a Typical Error Calculation

The example given presumes the air calibration technique. If calibration is done with air saturated water, the relative humidity consideration (III-D) is eliminated. If the Winkler calibration method is used, Type III errors are deleted and replaced by the uncertainty attributable to the overall Winkler determination.

Data: Instrument calibrated at 25°C, elevation estimated at 2000 ft., ±500 feet, normal barometric pressure presumed, calibrated on the 0-10 ppm scale to 7.8 ppm.
Readings taken on the 0-5 ppm range at 4.5 ppm, temperature 20°C, Salinity of 20 ppt.

Type	Description	Calculations	Error ppm
IA	Linearity	= .01 x 4.5 ppm	.045
IB	Range change	= .01 x 4.5 ppm	.045
IC	Salinity	$= .025 \times 4.5 \text{ ppm} \times \frac{20 \text{ ppt}}{40 \text{ ppt}}$	.056
IIA	Probe Background	$= .005 \times (1 - \frac{4.5 \text{ ppm}}{7.8 \text{ ppm}}) \times 7.8 \text{ ppm}$	.016
IIB	Prb. Linearity	= .003 x 4.5 ppm	.014
IIC	Temp. Comp.	= .01 x 4.5 ppm	.045
IIIA	Temp. Measure	= .015 x 4.5 ppm	.068
IIIB	Pressure	= .017 x 4.5 ppm	.076
IIIC	Altitude	= .018 x 4.5 ppm	.081
IIID	RH	= .016 x 4.5 ppm	.072
		Maximum possible error =	.518 ppm
		Probable Error	±.259

Considering a statistical treatment of the probable error at any time for any instrument, it is likely that the actual error in any measurement will be about 1/2 of the possible error. In this case, the probable error is about ±.26 ppm out of a reading of 4.5 ppm or 5.8% of the reading.

SYSTEM MAINTENANCE

Probe

After several hundred hours of operation the oxygen probe will develop a smudge like deposit on the transparent surface near the gold cathode. The smudge should be removed by wiping with a clean towel or lab wipe. Flush the probe with KCl, or distilled water and apply a new membrane.

If the probe has dried out sufficiently for crystals of electrolyte to form under the membrane, these should be flushed out and the membrane should be replaced.

Bubbles in general are not a problem, however, if a large bubble forms inside the membrane, the membrane should be replaced.

If erratic operation is observed or a calibration is not stable, the membrane should be replaced.

If holes or wrinkles are observed in the membrane, it should be replaced.

Some other gases such as SO_2, halogens and H_2S react in the oxygen cell and poison the cell. Poisoning is evidenced by discoloration of the gold. The tarnish is removable by vigorous wiping with a soft cloth or lab wipe. If these efforts are unsuccessful, the probe should be returned to the YSI Service Department for refinishing. Attempts to refinish the cathode surface without special equipment may impair the probe stability.

If the cell has been operated for some time with a loose or

wrinkled membrane, the gold cathode may become plated with silver. In this event, cathode refinishing is required and the probe should be returned to the YSI Service Department.

Instrument Case

The instrument case is water resistant when properly closed. As a precaution against damaged gaskets or loose fittings, the instrument case should be opened and inspected for moisture whenever the instrument has been subjected to immersion or heavy spray. The instrument case is opened by removing the four screws on the rear cover and lifting the cover off.

Instrument Batteries

The instrument batteries are two "C" size carbon-zinc cells located inside the instrument at the end opposite the meter. These should be replaced when the RED LINE knob is at its extreme adjustment or at least annually. The amount of remaining adjustment is an indication of the battery condition. The batteries are replaced by removing the four screws on the rear cover of the instrument and removing the two batteries at the end of the instrument opposite the meter. When installing the new batteries the plus (+) end fits into the red washer of the battery holder. (See Figure 4.)

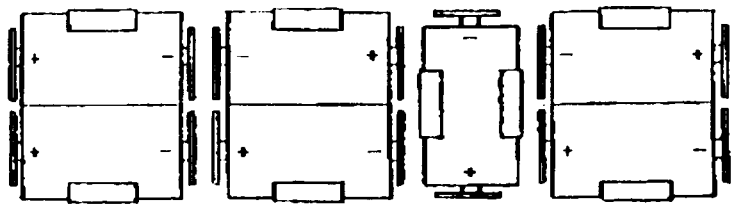
Submersible Stirrer Batteries

The stirrer batteries are installed by removing the instrument rear cover and installing the batteries in the five holders at the meter end of the instrument. The Plus (+) end of each battery fits into the red cup end of the battery holder. Exercise care to prevent accidental shorting of the batteries. As shipped, the batteries are charged and proper installation can be checked by switching the STIRRER knob to the BATT CHECK position. The meter should display at least 6.0

volts on the red 0-10 ppm scale. If there is no indication, the batteries should be checked for proper contact in their holders. If the reading is low, one battery may be reversed or one or all cells may require recharging. Plugging in the charger should immediately bring the meter reading to 6.0 volts or more if all cells are properly installed. (See Figure 4.)

The rechargeable batteries should have a service life of 500 to 1000 recharge cycles depending on variables of individual batteries and the conditions of charging and discharging. If the batteries will not hold a charge above 6.4 volts, one or all batteries may require replacement. The normal technique for locating a defective battery is to fully charge them and check the voltage of each battery with a voltmeter while operating the Submersible Stirrer. If an individual battery is generating less than 1.2 volts, it should be replaced. Batteries should be replaced in sets or with exact replacement types. Mixing different manufacture batteries can shorten the life of the set.

If any battery shows signs of leakage, it should be replaced.



DISPOSABLE CARBON ZINC INSTRUMENT BATTERIES

RECHARGEABLE NICKEL CADMIUM SUBMERSIBLE STIRRER BATTERIES

Figure 4

REPAIR AND REPLACEMENT PARTS

If you experience difficulty with a YSI product, it may be returned to the YSI Customer Service Department for repair, even if the Guarantee has expired. YSI maintains complete calibration and repair facilities for prompt servicing of all YSI products. Repair parts also are available from the YSI Customer Service Department or from your local YSI Dealer.

Yellow Springs Instrument Co., Inc.
Customer Service Department
P.O. Box 279
Yellow Springs, Ohio 45387, U.S.A.

GUARANTEE

The YSI Model 57 Dissolved Oxygen Meter, and all YSI oxygen probes and accessories designed for use with this instrument, are guaranteed for one year against defects in workmanship and components. Damage through accident, misuse, or tampering will be repaired at a nominal charge, if possible, when the instrument is returned to the factory.

In communications regarding this instrument, please mention model and serial number.

APPENDIX E

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
230 SOUTH DEARBORN STREET
CHICAGO, IL 60604

REPLY TO THE ATTENTION OF:

5HS-11

September 11, 1991

Mr. Kevin K. Wolka, P.E., Ph.D.
Geraghty & Miller, Inc.
50 W. Big Beaver Road
Troy, Michigan 48084

Dear Mr. Wolka:

Attached are the Standard Operating Procedures (SOPs) that are a part of the Quality Assurance Project Plan Addendum (QAPP Addendum) for the Ecological Assessment/Inventory Workplan for the Hi-Mill Manufacturing site, Highland, MI. The U.S. EPA has made corrections and gives approval on the corrected versions only. Please inform ENSECO laboratories that they are required to use the U.S. EPA corrected SOPs for the analyses. No changes are required for the SOP for Total, Fixed and Volatile Solids.

Please inform ENSECO that, with regard to comment 2b (referring to Section 10.2.1), they should try to achieve "90-110%" accuracy and "5%" precision as shown in the QAPP corrections. However, if the lab is unable to achieve the required accuracy and precision, the U.S. EPA must be informed as soon as possible.

Final approval of the entire Ecological Inventory/Assessment Workplan will be given as soon as we receive and review your responses to the comments dated September 5, 1991, and the replacement pages showing the change in laboratories. The responses will then be included as an addendum to the workplan and the replacement pages inserted before it is approved.

If you have any questions, please feel free to contact me at (312) 886-5993.

Sincerely,

Karla L. Johnson
Remedial Project Manager

cc: Steve Ellingson, Geraghty & Miller

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
230 SOUTH DEARBORN ST.
CHICAGO, ILLINOIS 60604

REPLY TO THE ATTENTION OF

5SMQA

MEMORANDUM

DATE: SEP 11 1991

SUBJECT: Approval of the PRP-Lead Quality Assurance Project Plan (QAPjP) Addendum for the Ecological Assessment Activity at the Hi-Mill Manufacturing Site in Highland, Michigan

FROM: Valerie J. Jones
Regional Quality Assurance Manager

TO: John Kelley, Acting Chief
Remedial and Enforcement Response Branch (5HS)

ATTENTION: Karla Johnson, Remedial Project Manager

I am providing approval of the subject PRP-Lead QAPjP addendum for the ecological assessment at the Hi-Mill Manufacturing site in Highland, Michigan. This approval is provided after we reviewed the SOPs, which were received by the Quality Assurance Section (QAS) on September 5, 1991 (QAS Log-In No. 1594).

Please note that, to facilitate the approval of this subject QAPjP, the following chnages, which were agreed during the September 10, 1991 conference call between QAS, WMD, Geraghty & Miller, and ENSECO laboratory representatives, was made by QAS staff:

1. In Section 8.1.8 of the QAPjP, the last sentence of the first paragraph was revised to read, "The results of chemical analysis of the sediment samples will be used to provided additional qualitative information on the levels and extent of inorganic contamination in target pond only."

2. SOP for the Determination of Total Organic Carbon (TOC) in Soil

   a. In Section 9.3, a statement, "Immediately, a separate aliquot (0.5 - 1.0 g) will be weighed into a preweighed crucible. Record the weight, and dry the sample in oven at 105°C until constant weight is obtained. Calculate the percent soild." is added.

   b. In Section 10.2.1, the accuracy and precision are changed from "85-115%" and "20%" to "90-110%" and "5%" respectively.

c. In Section 10.2.2, the control limit for standard checks was changed from "10%" to "5%".

d. In Section 11 (calculations), the equation was revised as follows:

$$mg/Kg\ C = \frac{0.04\ g}{\text{Sample Weight (g)}} \times \text{Instrument Reading (mg/Kg)}$$

where: Sample weight (g) = Actual Sample weight (g) x %Solid

e. Section 12.1 was revised to read, "Reporting units are mg/Kg on dry weight basis".

3. SOP for Measurement of pH in Soil

a. In Section 1.5 (Analysis Time), the description was revised to read, "Preparation time is about 30 minutes. Approximate analytical time is 5 minutes per sample."

b. In Section 5.2, the second sentence was revised to read, "Samples, however, must be analyzed within one hour of mixing with deionized water or calcium chloride solution."

c. Section 8.1.1 was revised to read, "Weigh 20 g sample into a 100 ml beaker and add 40 ml deionized water. Mix with constant stirring with a magnet stirrer for 30 minutes."

d. Section 8.1.2 and 8.2.2 were revised to read, "Immediately, the pH of the sample will be measured by inserting the electrode into the resulting paste as given in Section 8.3.2."

e. Section 8.3.2 was revised to read, "Insert the electrode into the resulting paste under stirring."

A copy of these revised pages is attached to this memo for your use, and they should be incorporated in the QAPjP and SOPs.

The original signature page is included. Please have the Remedial Project Manager provide final sign-off, and send us a copy of the completed signature page within two weeks of this approval memo.

Attachment

cc: Kaushal Khanna, TSU

SECTION 8.0
QUALITY ASSURANCE PROJECT PLAN
ADDENDUM
REMEDIAL INVESTIGATION/FEASIBILITY STUDY
HI-MILL MANUFACTURING COMPANY
Highland, Michigan

Prepared by:

GERAGHTY & MILLER, INC.
126 N. Jefferson St.
Suite 400
Milwaukee, WI 53202

Approved by:

Project Coordinator **Geraghty & Miller, Inc.**	Kevin Wolka	Date
Quality Assurance Officer **Geraghty & Miller, Inc.**	Tim Davis	Date
Quality Assurance Officer **USEPA Region V**		9/11/91 Date
Remedial Project Coordinator **USEPA Region V**	Karla Johnson	9/11/91 Date

CHANGED PAGES

been adversely impacted. Similar objectives apply to the aquatic inventory. To determine whether adverse ecological impacts have occurred in Target Pond samples of phytoplankton, zooplankton, and benthic macroinvertebrates will be collected. These samples will be collected from the sample locations used to collect the sediment samples. Upon receipt by the laboratory the different taxa in these communities will be identified and enumerated. At each sampling location and near the center of Target Pond and Waterbury Lake vertical profiles of water temperature, specific conductivity, and dissolved oxygen will be recorded.

The literature search will consist of accessing one or more databases to obtain information on the potential impacts of elevated levels of inorganic constituents on trees. Several trees near the Hi-Mill Manufacturing Company have died. Information obtained during the literature will be used to help evaluate whether the observed levels of inorganic constituents in soil and sediment samples from the site may have killed the trees.

8.1.8 Intended Data Usage

Data from the sediment toxicity evaluation will be used to help determine if the sediment in Target Pond is toxic to benthic macroinvertebrates. The qualitative inventory of benthic macroinvertebrates will also be used to help determine if changes have occurred in the composition or numbers of benthic organisms at the sampling locations in Target Pond. A determination of toxic impacts to the overlying water column will be assessed by qualitatively evaluating the composition and number of phytoplankton and zooplankton. The chemical analysis of the sediment samples will be used to provided additional qualitative information on the levels and extent of inorganic contamination in target pond only." Field measurements of dissolved oxygen will provide information on the potential mobilization of inorganic constituents from the sediment and the threat of anoxia to the aquatic fauna. Specific conductivity and water temperature will assist in determining if the water-bodies are chemically or thermally stratified.

9.3 Place about 0.04 g homogenized sediment in the combustion boat and reweigh. Record the weight. Combustion boats should not be handled with the bare hand during this process (use forceps). If total carbon or inorganic carbon is to be determined, cupric oxide fines may be added to the sample to assist in combustion.

Immediately, a separate aliquot (0.5 - 1.0 g) will be weighed into a preweighed crucible. Record the weight, and dry the sample in oven at 105°C until constant weight is obtained. Calculate the percent soild.

9.4 Slide the boat into the furnace.

9.5 Press the start button.

9.6 The result is recorded as total organic carbon.

9.7 Samples which are high in TOC (greater than 4000 mg/kg) are diluted by weight with silica gel. To obtain a homogenous mixture, weighed soil samples are ground with a weighed portion of silica gel to a homogenous powder. An aliquot of around 0.04 g is taken from the diluted sample for analysis.

10. QA/QC Requirements

10.1 QC Samples

10.1.1 Analyze a blank, which is a "baked" boat and 40 mg silica gel, with 40 uL of DI water added with every batch of 20 or less samples.

10.1.2 Two DCS samples are required with every batch of 20 or less samples.

10.1.3 Check standards are required after every 10 or less samples and at the end of the run.

10.1.4 Duplicates may be required as project specific QC.

10.1.5 Spikes may be required as project specific QC. Inject 40 uL of 1000 mg/L stock onto the soil sample in the boat. The spiking concentration is 1000 mg/kg.

10.1.6 If dilutions are needed run a silica gel blank along with the samples.

10.2 Acceptance Criteria

10.2.1 DCS

	Accuracy	Precision
TOC	90-110%	5%

10.2.2 Standard checks must be within 5% of the expected value.

10.2.3 Blanks must be less than two times the reporting limit.

10.3 Corrective Action Required

10.3.1 Verify that the instrument is properly calibrated.

10.3.2 Check gas flows with a flow meter at various points through out the system. Repair any leaks.

10.3.3 Check for non-linearity and also the IR output. If results are erratic the cell may need cleaning.

11. Calculations

$$\text{mg/Kg C} = \frac{0.04\ \text{g}}{\text{Sample Weight (g)}} \times \text{Instrument Reading (mg/Kg)}$$

where: Sample weight (g) = Actual Sample weight (g) x %Solid

Multiple by any dilutions made to get the final result.

12. Reporting

12.1 Reporting units are mg/Kg on dry weight basis

12.2 Reporting Limits

Samples less than 100 mg/kg are reported as ND.

12.3 Significant Figures

Three significant figures are reported.

13. References

13.1 EPA Method 415.1

13.2 SW-846 Method 9060

13.3 Dohrmann DC-80 Total Organic Carbon Systems Manual Edition 11.

1.4 Dynamic Range

The normal range is from 1 to 10 pH units. Errors at higher pH may be reduced by using a low-sodium-error electrode.

1.5 Analysis Time

Preparation time is about 30 minutes. Approximate analytical time is 5 minutes per sample

2. Method Summary

The sample is mixed with deionized water; if calcareous (high calcium containing) soil samples are being analyzed, a calcium chloride solution is used instead of water. The pH is then measured electrochemically.

3. Comments

3.1 Interferences

3.1.1 Incorrect results may occur at very high (>10) or very low (<1) pH. Errors at high pH may be reduced by using a low-sodium-error electrode.

3.1.2 Temperature fluctuations will cause measurement errors.

3.1.3 Oil may coat the electrode and interfere with response.

3.2 Helpful Hints

3.2.1 pH values of soils in 0.01M $CaCl_2$ tend to be just slightly lower than but highly correlated with those in water.

4. Safety Issues

4.1 All employees are expected to be familiar with and follow the procedures outlined in the Enseco/RMAL safety plan. Lab coats and safety glasses are required in all laboratory areas at all times. If you have any questions or safety concerns, see your supervisor or safety officer.

4.2 All samples should be considered potentially hazardous and handled with appropriate caution. Wear gloves and handle in a hood as much as possible.

5. Samples Collection, Preservation, Containers, and Holding Times

   5.1 Samples are to be collected in suitable wide-mouth containers and stored at 4°C.

   5.2 There is no holding time for pH on soil samples. Samples, however, must be analyzed within one hour of mixing with deionized water or calcium chloride solution.

6. Apparatus

   6.1 pH meter and electrodes. A combination electrode may be used.

   6.2 Beakers and other miscellaneous apparatus and glassware.

   6.3 Glass wool.

7. Reagents and Standards

   7.1 Buffers -- pH 4, 7, and 10. Obtain commercially.

   7.2 Calcium Chloride, 0.01 M

   Dissolve 1.47 g Calcium Chloride Dihydrate in deionized water and dilute to 1000 mL. Check the pH and adjust if necessary to between 5 and 6.5 with calcium hydroxide or hydrochloric acid. The conductance of this solution should be 2320 ± 80 umho/cm at 25°C.

   7.3 DCS (Duplicate Control Sample)

   Obtain a reference material with a certified value for pH. Sources include NTIS and various commercial suppliers. The true value for this material will vary from source to source, but must be established independently of the buffers used for calibration. For example, the minerals control sample from Environmental Resource Associates typically has a "true" pH of 9.2. The material is prepared according to the manufacturer's instructions.

8. Procedure

   8.1 Wastes, Oils, and Non-calcareous Soils

8.1.1 Weigh 20 g sample into a 100 ml beaker and add 40 ml deionized water. Mix with constant stirring with a magnet stirrer for 30 minutes.

8.1.2 Immediately, the pH of the sample will be measured by inserting the electrode into the resulting paste as given in Section 8.3.2.

8.2 Calcareous (high calcium containing) Soils

8.2.1 Weigh 10 g sample into a beaker and add 20 mL 0.01 M calcium chloride. Mix occasionally over the next 30 minutes.

8.2.2 Immediately, the pH of the sample will be measured by inserting the electrode into the resulting paste as given in Section 8.3.2.

8.3 Measurement of pH

8.3.1 Calibrate the pH meter using at least 2 buffers in the range expected for the samples (pH 4 and 7 for acidic samples, pH 7 and 10 for alkaline samples).

8.3.2 Insert the electrode into the resulting paste under stirring.

8.3.3 Allow the reading to stabilize and record the pH. Rinse the electrodes well between measurements.

9. QA/QC Requirements

9.1 QC Samples

9.1.1 The prep blank for soil pH is 40 mLs DI water. The blank should be prepped with the samples.

9.1.2 Two DCSs are required with each batch of 20 or less samples.

COPY OF SOPs WITH CHANGED PAGES INSERTED

Revised by QAS?USEPA on 09/11/91

STANDARD OPERATING PROCEDURE

Subject or Title: TOTAL ORGANIC CARBON IN SOILS & SEDIMENTS

SOP No.:	Revision No.:	Effective Date:
LM-RNA-1116	ORIGINAL	SEPTEMBER 3, 1991

Supersedes: N/A

ENSECO PROPRIETARY INFORMATION STATEMENT

1. Scope and Application

1.1 Analytes

This method covers the determination of total organic carbon using the Dohrmann DC-80 TOC analyzer.

1.2 The detection limit is 100 mg/kg.

1.3 Applicable Matrices

This method is applicable to soils, sludges, and sediments.

Prepared by: Anne Lang	Date: September 3, 1991
Management Approval:	Date: 9/3/91
QA Officer Approval:	Date: 9/3/91

1.4 Dynamic Range

Instrument response is linear to 4000 mg/kg. Higher concentrations may be analyzed by dilution of the samples.

1.5 Approximate analytical time is 5 minutes per sample.

2. Summary of Method

The sample is treated with HCL to drive off inorganic carbonates. Organic carbon in the sample is converted to carbon dioxide (CO_2) by catalytic combustion. The CO_2 formed is measured by an infrared detector. The amount of CO_2 is directly proportional to the concentration of carbonaceous material in the sample.

3. Comments

3.1 Oily samples will cause erratic results. This is minimized by homogenization of the sample.

4. Safety Issues

Follow normal laboratory precautions.

5. Sampling

Samples are collected in glass jars and kept at a temperature of 4°C and protected from sunlight and atmospheric oxygen.

6. Apparatus

6.1 Dohrmann DC-80 TOC Analyzer with sludge/sediment sampler.

6.2 Volumetric pipettes, volumetric flasks, beakers, etc.

7. Reagents and Standards

7.1 10% HCL

Carefully add 10 mLs of concentrated HCL to 90 mLs of deionized water.

7.2 Sodium Persulfate

Add 20 g of $K_2S_2O_8$ to 500 mL of deionized water. Add 1 mL concentrated HNO_3 and dilute to 1000 mL with deionized water.

7.3 TOC calibration Standard, 2000 mg/L

Dissolve 4.256 g potassium hydrogen phthalate in about 600 mL deionized water, add 2 mL concentrated sulfuric acid and dilute to 1000 mLs with deionized water.

7.4 DCS/ICB Solution, 1000 mg/L

Dissolve 2.128 g potassium hydrogen phthalate (use a chemical source independent from that used for the calibration standard) in about 600 mL deionized water, add 2 mL concentrated sulfuric acid, and dilute to 1000 mL with deionized water.

7.5 Silica Gel - baked in muffle furnace prior to use.

8. Procedure

8.1 Sample Prep

8.1.1 A 3-5 g representative aliquot of sample is air dried overnight.

8.1.2 Samples should be homogenized and ground to a very fine mesh. Leave out any extraneous artifacts, ie., glass chards, large twigs and leaves, etc.

8.1.3 On a watch glass add a few drops of 10% HCL to the dried, ground sample. If any fizzing occurs, saturate the sample slowly with 10% HCL. Redry sample. Test for fizzing again. Repeat until no fizzing or no inorganic carbon occurs.

8.1.4 Redry and regrind the sample.

8.2 Instrument Set-up

8.2.1 Turn on furnace and allow about 1/2 hour to warm up.

8.2.2 When furnace is up to temperature (as indicated by an intense red glow) adjust the oxygen to 200 cc/min and turn on the power switch to the detector unit.

8.2.3 Prior to running samples make sure that:

- Gas is coming into the UV reactor.
- Water column height difference in the U-tube is approximately 3-4". (This is typical back pressure indicator).
- UV lamp is turned off.
- The reactor is filled with sodium persulfate reagent.

8.2.4 Observe the baseline on the digital display. It should be stable after the furnace temperature is established and all the CO_2 is purged out of the reactor.

8.2.5 The platinum boat may accumulate carbonaceous impurities, mainly from the carrier gas. When the boat has been in the cool zone for a long period of time it should be placed in the furnace for at least two minute to "bake" before use.

8.2.6 Adjust Control Module Settings:

Mode Selection Switch: TOC
Sample Volume Select: 40 uL

8.2.7 Check instrument calibration by analyzing a 2000 mg/L standards. Inject 40 uL of this standard through the septum onto 40 mg of silica gel in the boat. Move the boat into the furnace and press the start button. If result is not within 10%, recalibrate. To erase prior calibration press the CALIB button for more than one second. Then repeat the procedure listed above for three injections of the 2000 mg/L standard. Be sure to let the boat cool for about a minute when removing from the furnace. Press CALIB button to recalibrate. Finally, run a 2000 mg/L standard to check calibration.

9. Analysis

9.1 Remove boat from the flip top inlet block.

9.2 Weigh the combustion boat and record the weight.

9.3 Place about 0.04 g homogenized sediment in the combustion boat and reweigh. Record the weight. Combustion boats should not be handled with the bare hand during this process (use forceps). If total carbon or inorganic carbon is to be determined, cupric oxide fines may be added to the sample to assist in combustion.

Immediately, a separate aliquot (0.5 - 1.0 g) will be weighed into a preweighed crucible. Record the weight, and dry the sample in oven at 105°C until constant weight is obtained. Calculate the percent soild.

9.4 Slide the boat into the furnace.

9.5 Press the start button.

9.6 The result is recorded as total organic carbon.

9.7 Samples which are high in TOC (greater than 4000 mg/kg) are diluted by weight with silica gel. To obtain a homogenous mixture, weighed soil samples are ground with a weighed portion of silica gel to a homogenous powder. An aliquot of around 0.04 g is taken from the diluted sample for analysis.

10. QA/QC Requirements

10.1 QC Samples

10.1.1 Analyze a blank, which is a "baked" boat and 40 mg silica gel, with 40 uL of DI water added with every batch of 20 or less samples.

10.1.2 Two DCS samples are required with every batch of 20 or less samples.

10.1.3 Check standards are required after every 10 or less samples and at the end of the run.

10.1.4 Duplicates may be required as project specific QC.

10.1.5 Spikes may be required as project specific QC. Inject 40 uL of 1000 mg/L stock onto the soil sample in the boat. The spiking concentration is 1000 mg/kg.

10.1.6 If dilutions are needed run a silica gel blank along with the samples.

10.2 Acceptance Criteria

10.2.1 DCS

	Accuracy	Precision
TOC	90-110%	5%

10.2.2 Standard checks must be within 5% of the expected value.

10.2.3 Blanks must be less than two times the reporting limit.

10.3 Corrective Action Required

10.3.1 Verify that the instrument is properly calibrated.

10.3.2 Check gas flows with a flow meter at various points through out the system. Repair any leaks.

10.3.3 Check for non-linearity and also the IR output. If results are erratic the cell may need cleaning.

11. Calculations

$$\text{mg/Kg C} = \frac{0.04\ \text{g}}{\text{Sample Weight (g)}} \times \text{Instrument Reading (mg/Kg)}$$

where: Sample weight (g) = Actual Sample weight (g) x %Solid

Multiple by any dilutions made to get the final result.

12. Reporting

12.1 Reporting units are mg/Kg on dry weight basis

12.2 Reporting Limits

Samples less than 100 mg/kg are reported as ND.

12.3 Significant Figures

Three significant figures are reported.

13. References

13.1 EPA Method 415.1

13.2 SW-846 Method 9060

13.3 Dohrmann DC-80 Total Organic Carbon Systems Manual Edition 11.

Revised by QAS/USEPA on 09/11/91

STANDARD OPERATING PROCEDURE

Subject or Title: pH (Soils and Wastes)

SOP No.: LM-RMA-1047	Revision No.: 3.1	Effective Date: 9/2/91

Supersedes: Rev. 3.0

1. Scope and Application

1.1 Analytes

This method is applicable to the determination of pH.

1.2 Reporting Limit

A reporting limit for pH is not defined.

1.3 Applicable Matrices

This method is applicable to wastes, oils and soils, both calcareous (high calcium containing) and non-calcareous. If there is uncertainty as to the type of soil being analyzed, the soil will be treated as non-calcareous.

Prepared by:	Date: 9/3/91
Management Approval:	Date: 9/3/91
QA Officer Approval:	Date: 9/3/91

1.4 Dynamic Range

The normal range is from 1 to 10 pH units. Errors at higher pH may be reduced by using a low-sodium-error electrode.

1.5 Analysis Time

Preparation time is about 30 minutes. Approximate analytical time is 5 minutes per sample

2. Method Summary

The sample is mixed with deionized water; if calcareous (high calcium containing) soil samples are being analyzed, a calcium chloride solution is used instead of water. The pH is then measured electrochemically.

3. Comments

3.1 Interferences

3.1.1 Incorrect results may occur at very high (>10) or very low (<1) pH. Errors at high pH may be reduced by using a low-sodium-error electrode.

3.1.2 Temperature fluctuations will cause measurement errors.

3.1.3 Oil may coat the electrode and interfere with response.

3.2 Helpful Hints

3.2.1 pH values of soils in 0.01M CaCl2 tend to be just slightly lower than but highly correlated with those in water.

4. Safety Issues

4.1 All employees are expected to be familiar with and follow the procedures outlined in the Enseco/RMAL safety plan. Lab coats and safety glasses are required in all laboratory areas at all times. If you have any questions or safety concerns, see your supervisor or safety officer.

4.2 All samples should be considered potentially hazardous and handled with appropriate caution. Wear gloves and handle in a hood as much as possible.

5. Samples Collection, Preservation, Containers, and Holding Times

5.1 Samples are to be collected in suitable wide-mouth containers and stored at 4°C.

5.2 There is no holding time for pH on soil samples. Samples, however, must be analyzed within one hour of mixing with deionized water or calcium chloride solution.

6. Apparatus

6.1 pH meter and electrodes. A combination electrode may be used.

6.2 Beakers and other miscellaneous apparatus and glassware.

6.3 Glass wool.

7. Reagents and Standards

7.1 Buffers -- pH 4, 7, and 10. Obtain commercially.

7.2 Calcium Chloride, 0.01 M

Dissolve 1.47 g Calcium Chloride Dihydrate in deionized water and dilute to 1000 mL. Check the pH and adjust if necessary to between 5 and 6.5 with calcium hydroxide or hydrochloric acid. The conductance of this solution should be 2320 ± 80 umho/cm at 25°C.

7.3 DCS (Duplicate Control Sample)

Obtain a reference material with a certified value for pH. Sources include NTIS and various commercial suppliers. The true value for this material will vary from source to source, but must be established independently of the buffers used for calibration. For example, the minerals control sample from Environmental Resource Associates typically has a "true" pH of 9.2. The material is prepared according to the manufacturer's instructions.

8. Procedure

8.1 Wastes, Oils, and Non-calcareous Soils

8.1.1 Weigh 20 g sample into a 100 ml beaker and add 40 ml deionized water. Mix with constant stirring with a magnet stirrer for 30 minutes.

8.1.2 Immediately, the pH of the sample will be measured by inserting the electrode into the resulting paste as given in Section 8.3.2.

8.2 Calcareous (high calcium containing) Soils

8.2.1 Weigh 10 g sample into a beaker and add 20 mL 0.01 M calcium chloride. Mix occasionally over the next 30 minutes.

8.2.2 Immediately, the pH of the sample will be measured by inserting the electrode into the resulting paste as given in Section 8.3.2.

8.3 Measurement of pH

8.3.1 Calibrate the pH meter using at least 2 buffers in the range expected for the samples (pH 4 and 7 for acidic samples, pH 7 and 10 for alkaline samples).

8.3.2 Insert the electrode into the resulting paste under stirring.

8.3.3 Allow the reading to stabilize and record the pH. Rinse the electrodes well between measurements.

9. QA/QC Requirements

9.1 QC Samples

9.1.1 The prep blank for soil pH is 40 mLs DI water. The blank should be prepped with the samples.

9.1.2 Two DCSs are required with each batch of 20 or less samples.

9.1.3 A standard check and a blank check are required after every 10 or less samples and at the end of the run. Any of the calibration buffers or DCS solution may be used for the standard check.

9.1.4 Duplicates may be required for project specific QC.

9.1.5 It is not possible to spike samples for pH.

9.1.6 See Enseco SOP M-EQA-002 and the Enseco QAPP for additional information.

9.2 Acceptance Criteria

9.2.1 DCS recovery must be 98 to 102%.

9.2.2 The RPD for DCS samples must be less than 5%.

9.2.4 Standard checks must be within 2% of the expected value.

9.2.5 There are no acceptance criteria for project specific QC.

9.2.6 See Enseco SOP M-EQA-002 for additional information.

9.3 Corrective Action Required

9.3.1 Check buffers and DCS to ensure that the expiration dates have not been exceeded. Replace solutions if necessary.

9.3.2 Check the electrodes and clean them if necessary. Replace filling solutions.

9.3.3 Check electrode slope. If less than 98% of theoretical Nernstian value, the electrode should be replaced.

9.3.4 Recalibrate the meter and recheck against DCS.

9.3.5 Reanalyze all affected samples.

9.3.6 Consult supervisor if problems persist.

10. Calculations

There are no calculations for pH.

11. Reporting Requirements

11.1 Results are reported in pH units.

11.2 Significant Figures

Report results to one decimal place (± 0.1 unit).

11.4 LIMS Data Entry

The usual standards for data entry apply.

12. References

12.1 Method source: SW-846 3rd Edition Method 9045, ASTM D 2110-78(B).

12.2 Additional Information: Methods of Soil Analysis, 2nd Edition

12.3 Deviations from source method and rationale
The calcium chloride solution is not initially prepared as a concentrate. It is not standardized against silver nitrate.

12.4 Oily samples are handled by procedures based on ASTM D2110-78(B), pH of Water Extracts of Halogenated Organic Solvents and Their Admixtures. Deionized water is used instead of boiled distilled water, and phase separation is achieved using glass wool rather than separatory funnels.

12.5 Related Documents:

12.4.1 LM-RMA-1071 pH, Alkalinity, Conductance (Autotitrator)

12.4.2 LM-RMA-1091 pH (Manual Method)

12.4.3 M-EQA-002 Internal QC Checks - Laboratory Performance QC

12.4.4 Enseco QAPP

12.5 Updates to SOP

Version 2.0 was updated to Version 3.0 to include provision for analysis of a prep blank.